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A new preconcentration procedure to quantify total acid hydrolyzed fluoride in selected beverages and foods by spectrophotometry

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A new micellar-mediated, cloud-point extraction (CPE) method has been developed for the quantification of trace levels of fluoride by means of spectrophotometry. The method is based on the selective ion association of stable anionic complexes, $Sn(OH)F_2^-$ or $Sn(OH)F_3^{2-}$ of fluoride with Sn(II) in presence of cationic dye (Nile blue A) at pH 5.0, and its extraction to the micellar-rich phase of nonionic surfactant polyoxyethylene (7.5) nonylphenyl ether (PONPE 7.5) as the extracting agent. Afterwards, the ternary complex formed was spectrophotometrically detected at 638 nm after preconcentration with CPE. Under optimized conditions, the calibration curves were rectilinear in the ranges of 5–25 and 25–360 μg L^{-1} in the linear region with changing sensitivity. The limits of detection and quantification (LOD and LOQ) ($3\sigma_{blank}/m$ and $10\sigma_{blank}/m$) was 1.45 and 4.83 μg L^{-1}, respectively, and the precision (as RSD) for determination of 15, 75, and 150 μg L^{-1} of fluoride was in the range of 2.35–4.65%. The validity of the method was checked through recovery experiments, independent analysis by potentiometry and analysis of the standard reference material SRM 2695. The developed method was successfully applied to the accurate, sensitive and reliable quantification of total acid hydrolyzed fluoride present in selected beverage and food samples.

1. Introduction

Fluoride is an essential trace microelement for human health at low levels and is a potentially toxic element at higher levels.[1] Too little fluoride in the diet leads to caries, especially in young children. On the other hand, its compounds are quite toxic at high concentrations because they can cause blocking of various enzymes.[2] Because fluoride is required for growth, healthy bone tissue and teeth, it is added to drinking water and toothpaste.[3] The daily consumption of fluoride of adults and children should be in the range 0.20–0.35 g and 1.5–4.0 mg L^{-1} for fluoride per kilogram of body weight.[4,5] If this value is exceeded, skeletal fluorosis and other bone diseases may occur.[6] Therefore, there is a great need to develop a simple, sensitive, selective and inexpensive method for the detection and continuous monitoring of trace amounts of fluoride in beverage samples.

Fluoride detection has been mostly performed using analytical techniques such as ion-selective electrodes (ISE),[7] ion chromatography (IC) after microwave-induced combustion,[8] capillary zone electrophoresis (CZE),[9] and potentiometric determination.[10] A disadvantage of these methods is that they are time consuming because results of the methods are adversely affected by interference products that form by interaction between anions and cations in samples.[3] Moreover, there are many analytical fluorine methods such as continuous powder introduction, microwave-induced plasma optical emission spectrometric (CPI-MIP-OES);[11] high-resolution, continuous-source molecular absorption spectrometry (HR-CS-MAS);[12] solid sampling, graphite-furnace molecular absorption spectrometry (SS-GF-MAS);[13] inductively-coupled plasma, optical emission spectrometry (ICP-OES);[14] laser-excited, molecular fluorescence spectrometry (LEMOFS);[15] total reflection X-ray fluorescence spectrometry (TXRF);[16] electrothermal vaporization inductively-coupled plasma mass spectrometry (ETV-ICP-MS);[17] and electrothermal atomic absorption spectrometry (ET-AAS).[18] Determination of fluoride *via* these methods that are expensive and time consuming is extremely difficult because fluoride has high electronegativity values due to its high ionization potential of 17.42 eV and its resonance line corresponds to vacuum-UV region (90 nm).[3] Among these methods, spectrophotometric and spectrofluorimetric methods, which are widely used in the direct or indirect determination of fluoride, are based on the reaction of fluoride with coloured metal chelate complexes, producing either a mixed-ligand ternary complex or replacement of the ligands, such as SPANDS, xylenol orange, hemicyanine, quercetin and 3-hydroxy-2-sulfoflavone,[19–23] by fluoride to give a colorless metal–fluoride complex and the free ligand with a different color of the metal–ligand complex, allowing detection limits at sub-ppm levels with specific self-advantages and disadvantages. Therefore, there is still a need to search highly sensitive and selective

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indicator dyes that can be applied in the detection of fluoride at trace levels.

For these purposes, UV-Vis spectrophotometry is still widely used in analytical chemistry. Moreover, this tool has advantages over other methods, including simplicity, low cost, accuracy, selectivity, rapidity and no need for expert users. Because the quantity of fluoride in food and beverages is very low, a separation and preconcentration method should be applied prior to analysis. Among separation and preconcentration methods, cloud-point extraction (CPE) will continue to be attractive. The reason for this interest is CPE's "green chemistry" properties such as surfactants that are nontoxic, not volatile, and not easily flammable, unlike organic solvents used in liquid–liquid extraction; use of dilute solutions in experiments, an inexpensive process compared to organic solvents; and the generation of few laboratory residues.[24] Also, CPE enables higher recovery efficiency and a large preconcentration factor. Micelles-assisted extraction methods have a wide range of applications in several different matrices in analytical chemistry.

The main aim of the present work was to develop a rapid, accurate and reliable method for separation and preconcentration of total fluoride in food and beverages using the CPE technique prior to its detection *via* UV-Vis spectrophotometry. The method is based on the selective ion association of stable anionic complexes, $Sn(OH)F_2^-$ or $Sn(OH)F_3^{2-}$ of fluoride with Sn(II) in the presence of cationic dye, Nile blue A ($NBAH^+$) at pH 5.0, and its extraction to the micellar phase of nonionic surfactant polyoxyethylene (7.5) nonylphenyl ether (PONPE 7.5) as the extracting agent. The proposed method was successfully applied to the determination of total acid hydrolyzed fluoride at trace levels in selected beverage and food samples after preconcentration with CPE as well as analysis of a standard reference material (SRM 2695).

2. Experimental

2.1 Instrumentation

Absorbance measurements at the selected wavelengths, 638 and 635 nm with and without preconcentration with CPE, respectively, were conducted on a double-beam UV-visible spectrophotometer (Shimadzu UV-1800 PC, Kyoto, Japan) equipped with 1.0 cm quartz cells. The fluoride concentration was also quantified using a fluoride ion-selective electrode (ISE DC219F, Mettler Toledo) for evaluation of result reliability. A centrifuge (Universal-320, Hettich Centrifuges, England) was used to accelerate the phase separation process; and a thermostatic water bath (EPC 4420, Thermal, Istanbul, Turkey) to maintain the temperature in CPE experiments. The pH measurements were carried out with a pH meter (pH-2005, JP Selecta, Spain); Eppendorf vary-pipettes (10–100 and 200–1000 μL) were used to deliver accurate volumes. An ultrasonic cleaner (UCS-10 model, Jeio Tech, Co., Ltd., Seoul, Korea), as well as a microwave oven (MLS-1200 Mega, Milestone, Sorisole, Italy) at maximum power of 1000 watts were used to de-gas and digest food samples and beverages with and without alcohol. Samples were refrigerated to keep them fresh and cool until the analysis.

2.2 Chemicals and reagents

All chemicals and reagents were of analytical-reagent grade or higher purity. Ultra-pure water with a resistivity of 18.2 MΩ cm was prepared using a Labconco (USA) water purification system. All solutions were prepared with the ultra-pure water. A stock solution of fluoride (1000 mg L^{-1}) was prepared by dissolving the appropriate amount of sodium fluoride from Sigma (St Louis, MO, USA) in the water. Stock solution of 1.0×10^{-3} mol L^{-1} $NBAH^+$ (Sigma) was prepared fresh daily by dissolving the reagent in ethanol (Merck) and diluting with ultra-pure water. The stock solution of 1000 mg L^{-1} Sn(II) was prepared by dissolving 1.94 g of $SnCl_2 \cdot 2H_2O$ supplied by Merck (98% [w/w]), in 2.0 mol L^{-1} HCl solution while heating, and then completing to 1000 mL with the water. The solution of 2.5% (v/v) of PONPE 7.5 (Sigma) was prepared by mixing 2.5 mL of surfactant with 25 mL ethanol in a flask of 50 mL and diluting 50 mL with the water. For the preparation of 100 mL of 0.1 mol L^{-1} pH, 5.0 citrate buffer solution, 20.5 mL of 0.1 mol L^{-1} citric acid (Merck) and 29.5 mL of 0.1 mol L^{-1} sodium citrate (Merck) solutions were mixed and diluted to 100 mL with the water. All the prepared stock solutions were stored in polyethylene bottles in a refrigerator at 4 °C. The vessels and pipettes used for trace analysis were kept in 10% (w/v) HNO_3 for at least 24 h and subsequently washed five times with the water.

2.3 Preparation of CRMs, beverage and food samples for analysis

For the present study, nine non-alcoholic and three alcoholic beverages, and five soup mix samples of different brands were randomly selected. All samples were obtained at a local supermarket in Sivas, Turkey. First, all of the glassware and other mineralization containers used were washed in 10% (v/v) HNO_3 to avoid contamination. In order to minimize contamination risk and analyte loss, and thus to ensure reliability of obtained results, initially microwave- and ultrasonic-assisted extraction procedures were adopted and used in parallel in the analysis of fluoride as a fast, efficient, cost-effective and reliable digestion tool in the sample preparation step.

The steps of the first digestion (microwave power) process follow: to evaluate the optimal microwave parameters for the quantitative extraction of fluoride, 10 mL solutions of HNO_3 changing in 2–20% (v/v) were added to the representative beverage or food samples and irradiated at different microwave power and time settings. Corresponding process blanks and standards were also subjected to the general microwave-assisted digestion procedure in order to check possible contamination and loss of analyte. The results obtained were compared with those obtained for the non-irradiated solutions. The corresponding process blank solution was used for preparation of standard fluoride solutions for spectrophotometric measurements as matrix-matched standards. An accurately measured amount (2–10 mL or 0.2–1.0 g) of beverage or food sample, with calibration sensitivity of ±0.1 mL and ±0.1 mg, was transferred into a microwave digestion glass vessel and 10 mL extractant solution (12% (v/v) HNO_3) was added. After thorough mixing of the sample with the extractant, the vessels were closed and kept

in the microwave oven and subjected to microwave irradiation for 30–240 s at 150–750 W power. After completion of the extraction processes, the microwave vessel was allowed to cool to room temperature and the supernatant was separated from the sample matrix by centrifugation for 5 min at 3500 rpm. After centrifugation, the clear supernatant was transferred to another precleaned 50 mL tube, and then the sample extracts were brought to volume with deionized water for preconcentration of the trace fluoride with CPE before detection *via* spectrophotometry at 638 nm. Each sample was processed in three replicates and each replicate was measured twice. Based on previous studies, the optimal conditions obtained for microwave-assisted extraction of fluoride from two sample matrices follow: extractant concentration, 12% (v/v) HNO_3; liquid and solid sample amounts, 5 mL and 0.6 g; microwave irradiation time, 180 s; and microwave power, 450 W.

The steps of the second digestion (ultrasonic power) process follow: (1) 20 mL of the samples were transferred into a 150 mL beaker. (2) The samples were added to 15 mL of diluted HNO_3 (1.5 mol L^{-1}) and 10.0 mL of diluted H_2O_2 (1.0 mol L^{-1}) (3 : 2, v/v). (3) The final volume of the mixture was completed to 100 mL with the ultra-pure water. (4) The prepared mixtures were initially heated in an ultrasonic bath for 10 min at 40 °C (300 W, 60 Hz) until a clear/transparent solution was obtained. (5) The pH of the digested samples was adjusted to 7.0 by using diluted NaOH (2 mol L^{-1}). (6) After centrifugation at 4000 rpm for 5 min, the digested samples were filtered using a membrane filter (0.21 μm pore diameter) into a volumetric flask before analysis. Digests of samples were clear and colorless solutions. Finally, the total fluoride contents of all samples were determined by using the three-point standard addition approach in order to suppress the matrix effect by means of UV-Vis spectrophotometry after separation and preconcentration with CPE under optimized conditions. Also, two SRMs were studied in order to verify the accuracy and precision of the proposed method. The selected SRMs with matrix matches are SRM 2695 fluoride in vegetation with low and high levels. The certified values are available for fluoride for assessment of method accuracy. The SRMs were also submitted to similar digestion processes. Samples were directly analyzed by using both the proposed method and potentiometric detection method for reliability of obtained results after dilution at suitable ratios. All points in optimization step and calibration curves before and after CPE were run in triplicate, and results indicated with error bars. The one- and two-paired ANOVA tests in optimization and analysis steps of samples were conducted for statistical comparisons.

2.4 The general CPE procedure

An aliquot of the sample or standard solution containing fluoride in the ranges of 5–25 and 25–360 μg L^{-1}, 1.2×10^{-3} mol L^{-1} citrate buffer at pH 5.0, 2.5×10^{-5} mol L^{-1} $NBAH^+$, 1.2 mg L^{-1} Sn(II), 1.5×10^{-3} mol L^{-1} KNO_3 and 0.08% (v/v) PONPE 7.5 were mixed in a centrifuge tube having a final 50 mL volume. The solutions were then mixed well and kept in a thermostatic water bath for 15 min at 40 °C. The phase separation was accelerated by centrifuging at 4000 rpm for 5 min. Next, the mixture was cooled in a refrigerator for 5 min in order to increase viscosity of the surfactant-rich phase and facilitate removal of the aqueous phase. Then, the aqueous phase was easily separated from surfactant-rich phase by inverting the tube. Then, the surfactant-rich phase was diluted to 0.8 mL with methanol in order to reduce its viscosity prior to spectrophotometric detection at 638 nm. Finally, the amounts of fluoride in beverage and food samples were determined by using either the direct calibration curve or standard addition method in order to suppress the possible matrix effect.

3. Results and discussions

3.1 General considerations related to method development

The method is based on the selective ion association of $Sn(OH)F_2^-$ or $Sn(OH)F_3^{2-}$ ions produced depending on concentration of fluoride in presence of excess Sn(II) ions with Nile blue A at pH 5.0, and then extraction of ternary complex to micellar phase of nonionic surfactant polyoxyethylene (7.5) nonylphenyl ether (PONPE 7.5) as the extracting agent. The extracted surfactant-rich phase is diluted with methanol, and its absorbance of ternary complex, which is linearly related to fluoride concentration, is spectrophotometrically measured at 638 nm in the presence of KNO_3 as the salting-out agent. Therefore, as a result of the selective anionic $Sn(OH)F_2^-$ or $Sn(OH)F_3^{2-}$ complexes formed depending on fluoride concentration due to hydrolysis of Sn^{2+} ions at pH 5.0,[25–27] the ion-association complex of positively charged Nile blue A, $NBAH^+$ assisted by PONPE 7.5 micelles can be extracted by the CPE method (Fig. 1). Thus, for further applications the variables affecting CPE efficiency were optimized to achieve maximum sensitivity.

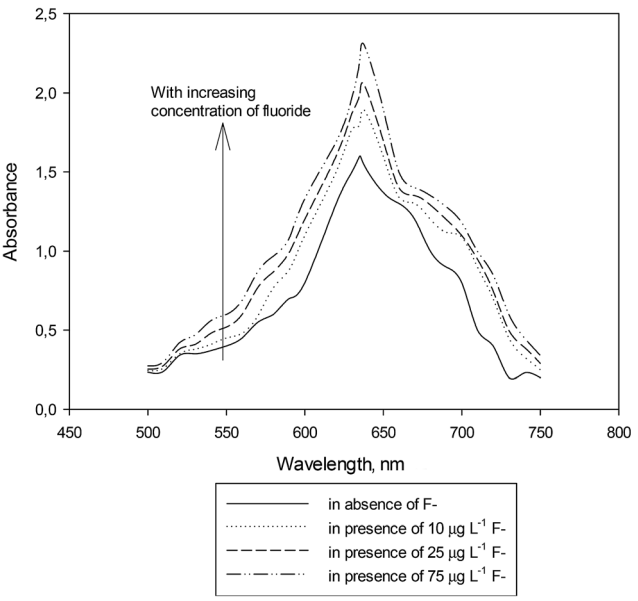
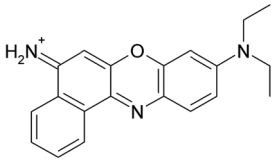


Fig. 1 Absorption spectra of ternary complex at three different concentration levels. Optimal conditions: 1.2×10^{-3} mol L^{-1} citrate buffer solution at pH 5.0, 2.4×10^{-5} mol L^{-1} $NBAH^+$, 1.2 mg L^{-1} Sn(II), 1.6×10^{-3} mol L^{-1} KNO_3 and 0.08% (v/v) PONPE 7.5 with thermostatic water bath at 40 °C for 15 min and centrifugation time of 5 min at 4000 rpm.

Nile blue A is a fluorescence-sensitive dye exhibiting a low emission intensity below pH 3.0, and enhanced emission above pH 8.0. The open molecular structure of the dye, which is also known as 5-amino-9-diethyliminobenzo[*a*]phenoxazonium perchlorate, may be represented as follows:



The dye is soluble in acid and alkaline solutions, and partially soluble in water. In a wide pH range of 4–10, it is present in mono-cationic form, NBH^+, due to its dissociation constants $pK_{a1} \sim 4.0$ and $pK_{a2} \sim 10.0$.[28] At pHs lower than 4.0, it becomes a di-cationic acidic form of dye, $NBAH_2^{2+}$, while it is in a relatively basic form, NBA, without charge at pHs > 10. However, in the pH 4–10 range, the mono-cationic form of the dye, $NBAH^+$ is stabilized by resonance. Due to this property, it is clear that the reagent tends to give an ion-association complex with anionic $Sn(OH)F_2^-$ or $Sn(OH)F_3^{2-}$ complexes, formed in the presence of Sn(II) ions at pH 5.0. Because of its high solubility in aqueous micellar media, in previous studies it was observed that the ion-association complex could efficiently be extracted into surfactant-rich phase above the critical micelle concentration (CMC) (0.085 mmol L^{-1}) of the nonionic surfactant, PONPE 7.5, with an optimum concentration of 0.08% (v/v) corresponding to a concentration of 1.31 mmol L^{-1}. To further improve the calibration sensitivity and selectivity of the method, the CPE has been explored using nonionic surfactant with KNO_3 as a salting-out agent to enhance the binding of hydrophobic complexes to the surfactant-rich phase. The CPE can efficiently be used when the targeted analytical species are hydrophobic in nature. Though the ion-association complex is water soluble, it has successfully been extracted into the surfactant-rich phase in the presence of the resonance-stabilized reagent, $NBAH^+$, at pH 5.0. The mechanism proposed for CPE of trace fluoride species in aqueous micellar medium assisted by PONPE 7.5 micelles can be explained by eqn (1)–(4):

$$Sn^{2+} + 3F^- + H_2O \rightarrow Sn(OH)F_2^- + HF \text{ at pH 4.0–6.0} \quad (1)$$

$$Sn^{2+} + 3F^- + H_2O \rightarrow Sn(OH)F_3^{2-} + H^+ \quad (2)$$

$$Sn(OH)F_2^- + NBAH^+ \rightarrow [Sn(OH)F_2^- \cdots NBAH^+]_{(\text{aqueous phase})} \leftrightarrow [Sn(OH)F_2^- \cdots NBAH^+]_{(\text{micellar phase})} \quad (3)$$

$$Sn(OH)F_3^{2-} + 2NBAH^+ \rightarrow [Sn(OH)F_3^{2-} \cdots 2NBAH^+]_{(\text{aqueous phase})} \leftrightarrow [Sn(OH)F_3^{2-} \cdots 2NBAH^+]_{(\text{micellar phase})} \quad (4)$$

3.2 Effect of pH and buffer concentration on CPE efficiency

The separation and preconcentration of fluoride by the CPE method involves previous formation of a stable complex, which needs to present sufficient hydrophobicity to be extracted into the small volume of the surfactant-rich phase. The pH is a critical factor affecting both the reaction between fluoride and Sn(II) ions/ion-pairing ligand (Nile blue A), and the extractability of ion-pairing complex into the surfactant-rich phase. Thus, in this part of experiment, the effect of different buffers such as citrate, phthalate, phosphate and universal Britton–Robinson were extensively studied for the extraction and detection of fluoride in the surfactant-rich phase in the range pH 2.0–7.0. As seen in Fig. 2a, the maximum absorbance was obtained with the citrate buffer system at pH 5.0 with a significant sensitivity difference compared to those of phthalate buffer at pH 4.0. This sensitivity

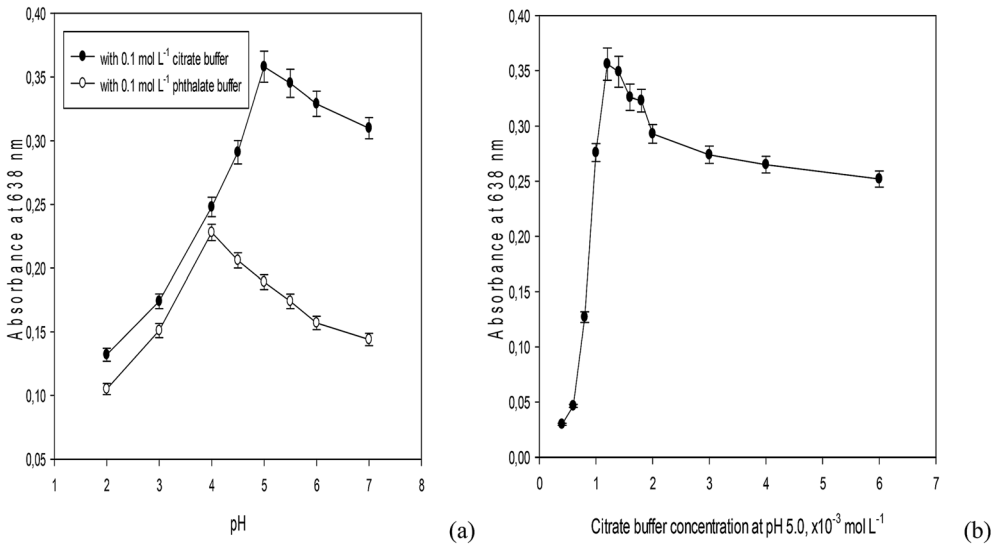


Fig. 2 Effect of (a) pH and (b) citrate buffer concentration on CPE efficiency. Optimal conditions: 25 μg L^{-1} F^-, 2.4×10^{-5} mol L^{-1} $NBAH^+$, 1.2 mg L^{-1} Sn(II), 1.6×10^{-3} mol L^{-1} KNO_3, and 0.08% (v/v) PONPE 7.5, with thermostatic water bath at 40 °C for 15 min and centrifugation time of 5 min at 4000 rpm.

difference may be due to the formation of a more stable complex of Sn(II) with citrate ions as a stabilizing buffer component to prevent the transformation of Sn(II) to Sn(IV) in presence of fluoride at pH 5.0. It is also implied in the literature[29] that Sn(II) gives highly stable complexes, $SnHCitrate^{-}$ and $SnCitrate^{2-}$, with log β of 10.3 and 19.5 in the presence of citrate ions at pHs $\geq$ 4.0. Below the pH 5.0, extraction efficiency is very low because complex formation is inadequate as a measure of protonation of ligand, NBA and dimerization equilibrium depending on pH, $2NBH^{+} \leftrightarrow (NBH)_2^{2+}$. It is implied in the literature[30,31] that the dye in low concentrations of 3.94×10^{-5} mol L^{-1} at pH $\leq$ 7.0 is aggregated with a dimerization constant of K_D: 5.31. Another reason for the reduction in absorbance may be aggregation of F^{-} (H_2F_2 with a pK_a value of 3.2) and Sn^{2+} ions (in forms of $Sn_2(OH)_2^{2+}$ and $Sn_3(OH)_4^{2+}$) at pHs < 4.0. However, at pHs > 5.0, the reason for the decrease in extraction efficiency can be deprotonation of ligand $NBAH^{+}$ to NBA with increasing OH^{-} ions.

Hence, an optimal value was selected as a pH of 5.0 in order to give the highest sensitivity. Furthermore, the effect of buffer concentration on the analytical signal was studied in the range of (0.5–6.0) $\times 10^{-3}$ mol L^{-1} concentration in Fig. 2b, and the best analytical signal was obtained using 1.2×10^{-3} mol L^{-1} of buffer solutions. Therefore, the buffer concentration of 1.2×10^{-3} mol L^{-1} at pH 5.0 was used as an optimal value for further studies.

3.3 Effect of concentration of ion-pairing reagent and Sn(II) on CPE efficiency

The CPE efficiency depends on the hydrophobicity of ion-pairing reagent and the complex formation. Nile blue A is a highly chromogenic and fluorogenic ion-pairing agent especially due to its resonance stabilized phenoxazine group containing hetero-nitrogen and oxygen atoms including $-NH_2$ and $-N(C_2H_5)_2$ groups. Sn(II) in aqueous solution predominantly is present in forms of $Sn(OH)^{+}$ and Sn^{2+} ions at lower pHs than 4.0, is present in form of neutral $Sn(OH)_2$ in pH range of 4.0–10.0, whereas at higher pHs than 10.0, it is present in form of anionic $Sn(OH)_3^{-}$ or $Sn(OH)_4^{2-}$ depending on pH change. Nile blue A may sensitively and selectively bind F^{-} ions as anionic hydroxyfluoride complexes, $Sn(OH)F_2^{-}$ or $Sn(OH)F_3^{2-}$ formed after hydrolysis of Sn^{2+} ions in presence of PONPE 7.5 as extracting agent and KNO_3 as salting out agent at pH 5.0. In the present study, Nile blue A was selected as an ion-pairing reagent for fluoride in presence of Sn(II) due to contain a protonated resonance stabilized-phenoxazine group that can participate in pH-dependent complexation at pH 5.0.

The effect of $NBAH^{+}$ concentration on analytical signal intensity of fluoride was studied in range of (0.006–0.12) $\times 10^{-3}$ mol L^{-1} and the results are shown in Fig. 3a. It can be seen that the signal intensity of fluoride dramatically depends on the concentration of $NBAH^{+}$ in CPE system. With the increase in concentration of $NBAH^{+}$, the signal intensity increased in initial and the maximum signal intensity was achieved at 0.024×10^{-3} mol L^{-1}. After this value, the analytical signal for fluoride decreased. Thus, 2.4×10^{-5} mol L^{-1} $NBAH^{+}$ was selected for further studies. The reason of decrease in absorbance may be aggregation of $NBAH^{+}$ with a dimerization constant of 5.31 at higher concentrations than 2.4×10^{-5} mol L^{-1}.

The variation of the analytical signal as a function of the concentration of the Sn(II) in the presence of 25 μg L^{-1} fluoride was studied in range of (0.2–4.0) mg L^{-1}, and the experimental results in Fig. 3b indicated that the signal intensity of the analyte linearly increases with Sn(II) concentration up to 1.2 mg L^{-1}. The maximum signal intensity linearly decreased with increasing slope at the higher concentrations. The cause of this decrease in signal may be either complexation of Sn(II) based on acid–base interaction or redox reaction with $NBAH^{+}$ in absence

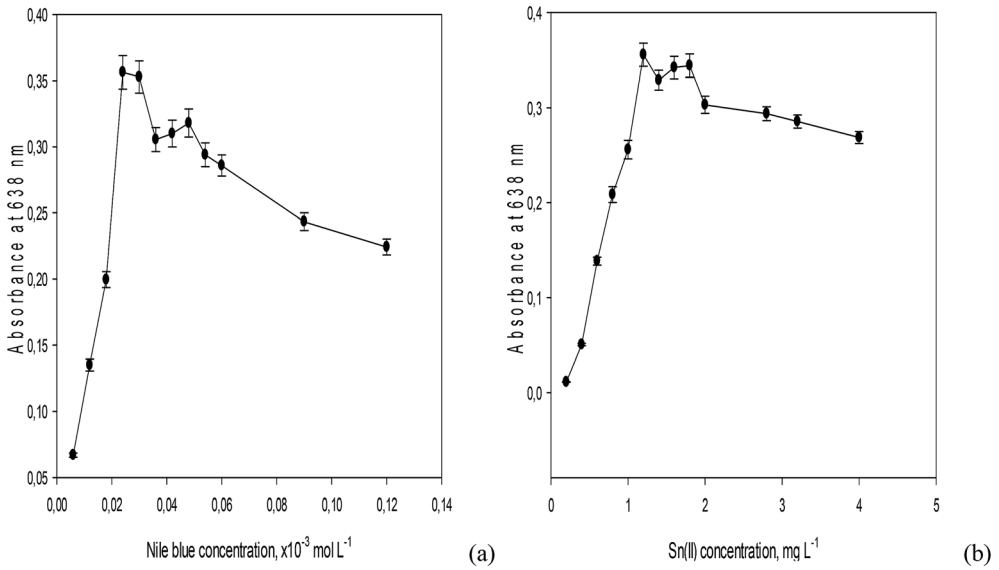


Fig. 3 Effect of concentrations of (a) $NBAH^{+}$ and (b) Sn(II) on CPE efficiency. Optimal conditions: 25 μg L^{-1} F^{-}, 1.2×10^{-3} mol L^{-1} citrate buffer at pH 5.0, 1.6×10^{-3} mol L^{-1} KNO_3, and 0.08% (v/v) PONPE 7.5, with thermostatic water bath at 40 °C for 15 min and centrifugation time of 5 min at 4000 rpm.

of fluoride due to increase in blank signal. So, 1.2 mg L^{-1} Sn(II) was selected as optimal value for further studies.

3.4 Effect of salting-out agent concentration on CPE efficiency

Studies on the effects of some additives, such as anionic, nonionic surfactants and inorganic electrolytes such as Na_2SO_4, KNO_3, NaCl, KCl and NH_4Cl on the cloud-point behavior of nonionic surfactants have been reported.[32–34] It was observed that the presence of electrolytes decreases the cloud point (salting-out effect), resulting in more efficient extraction. The lower cloud point is attributed to electrolytes promoting dehydration of the poly (oxyethylene) chains. According to Komaromy-Hiller *et al.*,[33] the salting-out phenomenon is directly related to desorption of ions to the hydrophilic parts of the micelles that increases interaction among micelles, and consequently leads to the precipitation of surfactant molecules. Based on this discussion, the influence of ionic salts strength such as NaCl, KNO_3, KCl, Na_2SO_4 and NH_4Cl on extraction efficiency was studied in the range of $(0.4–6.0) \times 10^{-3}$ mol L^{-1} under optimized reagent conditions in Fig. 4a. The maximum absorbance was obtained at 1.6×10^{-3} mol L^{-1} KNO_3 as a sensitivity enhancement salting-out agent. The absorbance considerably decreased with increasing KNO_3 concentration in the range of $(1.6–6.0) \times 10^{-3}$ mol L^{-1}. This effect might be explained by the additional surface charge when the KNO_3 concentration is very high, thus changing the molecular architecture of the surfactant and consequently the micelle formation process. It is necessary to emphasize that different blank solutions were also evaluated and no significant signal was obtained. Therefore, 1.6×10^{-3} mol L^{-1} KNO_3 was selected as the optimal value for further studies.

3.5 Effect of concentration of nonionic surfactants on CPE efficiency

In CPE choosing an appropriate surfactant is important, since the temperature corresponding to the cloud point is correlated with the hydrophilic property of a surfactant. A successful CPE should maximize extraction efficiency by minimizing the phase volume, thus increasing its concentrating capability. To the present, nonionic surfactants (mainly polyoxyethylenated alkylphenols, from PONPE 7.5, Tween-20 and Triton, such as Triton X-45 and X-114 series) are those most widely employed for metal analysis with CPE. The surfactants are commercially available, high purity grade, stable, and nonvolatile, relatively nontoxic and eco-friendly reagents. The variation of the analytical signal as a function of the concentration of nonionic surfactants Triton X-114, Triton X-45, Ponpe 7.5 and Tween 20 in the range of 0.02–0.2% (v/v) was also studied, shown in Fig. 4b. It is obvious that the best quantitative extraction was observed for PONPE 7.5 concentration of 0.08% (v/v). In this condition, it was observed that recovery of the analyte using a single-step extraction was quantitative. Therefore, 0.08% (v/v) Ponpe 7.5 was selected as the optimal value for further studies.

3.6 Effects of equilibrium temperature and incubation time

Equilibrium temperature and time are important parameters to complete complex formation quantitatively and achieve an easy phase separation and preconcentration on CPE. Hence, the effect of equilibrium temperature was studied in the range of 30–60 °C. As a result of experimental studies, the solutions became turbid as soon as they were placed in the water bath at temperatures >40 °C. The temperature had no significant effect on extraction efficiency, and the analytical signal remained constant at the temperature range of 30–60 °C. Higher temperatures led to

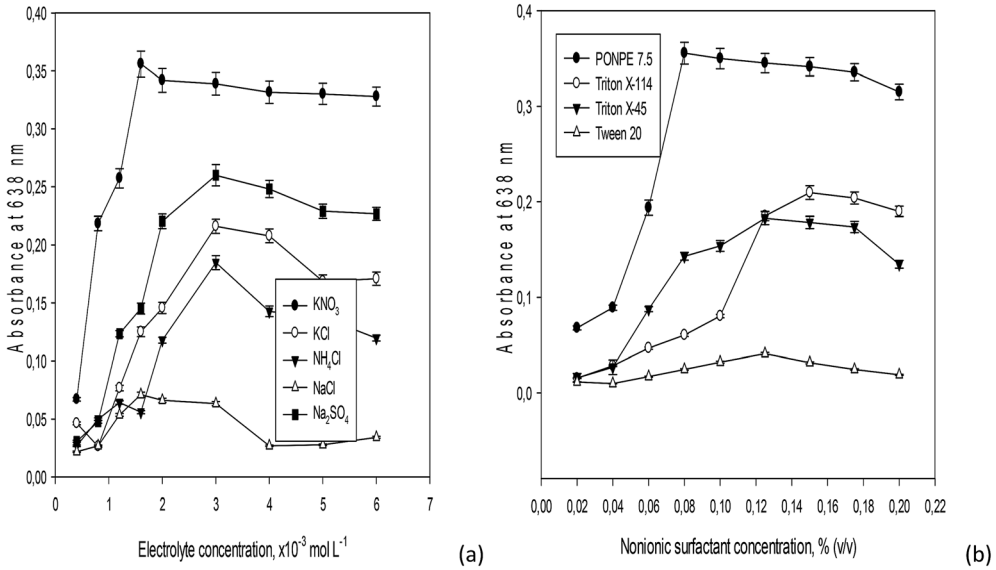


Fig. 4 Effect of concentrations of (a) electrolyte and (b) nonionic surfactant on CPE efficiency. Optimal conditions: 25 μg L^{-1} F^-, 1.2×10^{-3} mol L^{-1} citrate buffer at pH 5.0, 2.4×10^{-5} mol L^{-1} $NBAH^+$, 1.2 mg L^{-1} Sn(II), 1.6×10^{-3} mol L^{-1} KNO_3 with thermostatic water bath at 40 °C for 15 min and centrifugation time of 5 min at 4000 rpm.

Table 1 Analytical features of proposed CPE/spectrophotometric method

	Analytical features	
Parameters	After preconcentration, 638 nm	Before preconcentration, 635 nm
Analytical species	F^-, μg L^{-1}	F^-, μg L^{-1}
Linear ranges	5–25, 25–360	50–1500
Slope (m)	0.0194 ± 0.0016, $(2.66 \pm 0.12) \times 10^{-3}$	$(2.24 \pm 0.12) \times 10^{-4}$
Intercept (b)	-0.132 ± 0.0094, 0.2918 ± 0.0130	0.015 ± 0.0011
Regression coefficient, r^2	0.9940, 0.9972	0.985
Precision, RSD % (n: 5, 15, 75 and 150 μg L^{-1})	2.35–4.65	—
Recovery % (n: 5, 15, 75 and 150 μg L^{-1})	97.4–103.1	—
Detection limit[a] (n: 10, LOD, $3\sigma_{bos}/m$), μg L^{-1}	1.45	14.7
Quantification limit[a] (n: 10, LOQ, $10\sigma_{bos}/m$), μg L^{-1}[a]	4.83	49
Sensitivity enhancement factor[b]	86.6	—
Preconcentration factor[c]	62.5	—

[a] Ratio of analytical signal corresponding to 3- and 10-fold standard deviations of 10 replicate blank analyses to slope of calibration curve obtained after CPE. [b] Value calculated as ratio of calibration curve slopes obtained before and after preconcentration with CPE. [c] Value calculated as ratio of initial sample volume and final extracted volume (PF: 50 mL/0.8 mL: 62.5).

complex decomposition and reduction of complex extraction efficiency. Keeping the equilibrium temperature of 40 °C, the influence of incubation time on CPE was examined in the range of 2–30 min. It was observed that 15 min were sufficient to achieve a quantitative extraction of analyte. Thus, 40 °C and 15 min were chosen as the equilibrium temperature and incubation time for the CPE method, respectively.

3.7 Effects of centrifugation rate and time

Centrifuge time and rate are very important in the preconcentration of trace amounts of fluoride with high efficiency in a short time. Thus, under observed optimized conditions, the effect of centrifuge time and rate were studied in range of 2–20 min and 500–4000 rpm, respectively. The results showed that centrifugation for 5 min at 4000 rpm and cooling for 5 min in a refrigerator leads to maximum recovery and sensitivity for fluoride.

3.8 Effect of diluting agent

The volume of the surfactant-rich phase acquired after separation and preconcentration with CPE is small for detection with UV-Vis spectrophotometry. It is very important to choose the appropriate solvent for maximum extraction efficiency. The effect of various solvents such as methanol, acetonitrile, ethanol, acidic methanol, acidic ethanol, acetone and THF in the volume range of 0.5–2.0 mL was studied in order to dilute the surfactant-rich phase after phase separation. Based on results, the best regression coefficient, r^2 and analytical sensitivity, m/s_m, were obtained for the surfactant-rich phase diluted to 0.8 mL with methanol (with a phase volume ratio of 0.016) from calibration curves established for fixed fluoride concentrations of 25, 50 and 75 μg L^{-1}.

3.9 Calibration curve, detection limit and precision

Table 1 summarizes the analytical performance properties of the method with and without preconcentration with CPE such as linear ranges, slope, intercept, regression coefficient, precision, recovery, detection and quantification limits, enhancement and preconcentration factor. With preconcentration *via* CPE at 638 nm, the limits of detection and quantification defined as $3\sigma_{blank}/m$ and $10\sigma_{blank}/m$ (where σ_{blank} is the standard deviation of 12 replicate measurements of the blank and m is the slope of the calibration graph), LOD and LOQ,

Table 2 Effects of interfering matrix components on detection of 50 μg L^{-1} F^-

Interfering species	Tolerance limits
Na^+, K^+, NH_4^+, NO_3^-, HCO_3^-, thiourea, HPO_4^{2-}, Sr^{2+} and Mg^{2+}	>1000
Cl^-, Br^-, Cr^{3+}, Zn^{2+}, hydrazine, formaldehyde, citrate, tartrate, Mn^{2+}, Cd^{2+} and Co^{2+}	450–1000
Fe^{2+}, Ca^{2+}, oxalate, SCN^-, Ag^+, Pb^{2+}, Sn^{4+}, V^{5+}, Sb^{5+}, As^{5+} and Se^{4+}	250–450
Ni^{2+}, Mo^{6+}, V^{4+}, Mn^{3+}, As^{3+} and Sb^{3+}	75–200
Hg^{2+}, NO_2^- and S^{2-}	60
Si^{4+} and Fe^{3+}	35–50 (500[a])
$S_2O_3^{2-}$ and SO_3^{2-}	20–30 (350[b])
Bi^{3+} and Al^{3+}	10–15 (150[c])
IO_3^- and IO_4^-	5 (150[d])

[a] After masking with 250 μL of 0.05 mol L^{-1} CyDTA solution. [b] After pretreatment with 150 μL of 0.025% (w/v) formaldehyde solution. [c] After pretreatment with 250 μL of 1.0×10^{-3} mol L^{-1} thiourea solution. [d] After pretreatment with 100 μL of 0.025% (w/v) hydrazine hydrochloride solution.

Table 3 Fluoride contents of CRM obtained by using proposed CPE-spectrophotometric method

SRM	Sample amount, g	Replicate number, *n*	Certified value, μg g^{-1} F^-	By proposed CPE-spectrophotometric method: Found[a], μg g^{-1} F^-	Recovery %	RSD %	One paired Student's *t*-test[b]	*F*-variance test[b]
SRM 2695 fluoride in vegetation, high level	0.6	3	277 ± 10.9	280 ± 8.5[c], 278 ± 9.0[d]	101.1, 100.4	3.04, 3.20	0.61, 0.19	1.25, 1.11
SRM 2695 fluoride in vegetation, low level	0.6	3	64.0 ± 3.4	67.0 ± 2.5[c], 66.5 ± 3.0[d]	104.7, 103.9	3.73, 4.51	2.08, 1.44	1.44, 1.00

[a] Average and standard deviation of three replicate measurements at 95% confidence level. [b] Tabulated *t*-test and $F_{4,4}$ values for 4 degrees of freedom at 95% confidence level are 4.30 and 6.39, respectively. [c] Average and standard deviation of three replicate measurements at 95% confidence level after microwave-assisted digestion of samples. [d] Average and standard deviation of five replicate measurements at 95% after ultrasonic-assisted digestion of samples.

respectively, were 1.45 and 4.83 μg L^{-1} in rectilinear ranges of 5–25 and 25–360 μg L^{-1}. Without preconcentration *via* CPE at 635 nm, the limits of detection and quantification, LOD and LOQ, respectively, were 14.7 and 49 μg L^{-1} in the rectilinear range of 50–1500 μg L^{-1}. Sensitivity enhancement and preconcentration factors for fluoride were 86.6 and 62.5, respectively. The precision and accuracy of the method was controlled by the relative standard deviation (RSD) of five independent measurements taken from solutions containing all reagents including fluoride. The recovery rates and RSDs were in the range of 97.4–103.1% and 2.35–4.65% for three different concentration levels of 15, 75, and 150 μg L^{-1}, respectively.

3.10 Matrix effect

To evaluate the extraction efficiency of the method, interfering ions in different concentrations were added to a solution containing 50 μg L^{-1} of F^- and were investigated under optimized conditions. The tolerance limits of the different ions are shown in Table 2. The tolerance limit was identified as the concentration of added ions that caused greater than ±5.0% relative error. The interfering effects of interfering anionic and cationic species including $S_2O_3^{2}$, SO_3^{2-}, Bi^{3+}, Al^{3+}, IO_3^- and IO_4^- were efficiently removed by the addition of suitable masking agents to the solution before preconcentration with CPE. The method's superior performance for matrix components may be due to the high selectivity tendency of the ligand $NBAH^+$ in F^- ions in the presence of excess Sn(II) ions at pH 5.0.

4. Results for analysis of real samples

Method accuracy was controlled by analysis of the SRM 2695 fluoride in vegetation with low and high levels after dilution of samples digested under ultrasonic and microwave power so as to fall within the calibration range of detection methods (see Table 3). As seen in the table, the observed values (67.0 ± 2.5, 66.5 ± 3.0 μg g^{-1} for low fluoride levels and 280 ± 8.5, 278 ± 9.0 μg g^{-1} for high fluoride levels, *n*: 3), found by using CPE–UV-Vis for SRM, were statistically in good agreement with the standard values of 64.0 ± 3.4 and 277 ± 10.9 μg g^{-1}. As the standard values were within the 95% confidence interval about the mean of the experimentally determined values, there is no significant difference between the values. It can be concluded that the method is accurate, reliable and consequently free from systematic error. Also, in order to confirm the accuracy of the proposed method, a comparison method was independently used for three replicate measurements for the SRM. The results (68.0 ± 3.0 μg g^{-1} for low fluoride levels; 278 ± 9.5 μg g^{-1} for high fluoride levels, *n*: 3) found by using the reference method were in good agreement with the certified values. As a result, it has been found that the results found by both detection methods are highly quantitative in the 100.4–104.7% range with an RSD ranging from 3.04 to 4.51% for total acid hydrolyzed fluoride contents.

The applicability of the method was successfully investigated by determination of total fluoride in diverse beverages and food samples. Samples were pretreated by both microwave-assisted digestion and with the help of ultrasonic-assisted digestion, according to the procedure explained in Section 2.3. Prepared sample solutions of 5.0 mL were transferred into volumetric tubes of 50 mL individually. Then, the method in the linear range of 5–360 μg L^{-1} F^- was applied to determine quantities of total fluoride by using the standard addition method in order to suppress possible matrix effects. The results and recoveries for the samples spiked at concentrations ranging from 20 to 25 μg L^{-1} after dilution appear in Table 4. Recoveries from spiked solutions were quantitatively varied in the range of 95.0–99.2% for beverage samples and 97.2–102.4% for food samples with relative standard deviations of 2.4–4.7% and 2.6–4.3% (*n*: 5), respectively. As seen in Table 4, the student's *t*-test for comparison of mean values and their RSDs demonstrated that there was no significant difference between the mean values obtained by two digestion procedures at the 0.05 significance level. Because the experimental *t*-values ranging from 0.40 to 1.95 are lower than the tabulated *t*-value of 2.31, it can be concluded that the mean values obtained by two digestion approaches do not contain a significant difference for 8 degrees of freedom at the 95% confidence level. It is clear that the method for the samples has a good reproducibility as a measure of precision by variance analysis based on pooled standard deviation with experimental $F_{4,4}$ values ranging from 1.0 to 1.9. As a result, it is clear that the results found after microwave-

Table 4 Detection of total acid hydrolyzed fluoride levels of some alcoholic and nonalcoholic beverage and food samples, and percent recovery of spiked samples

	After microwave-assisted digestion (n: 5)					After ultrasonic-assisted digestion (n: 5)					
Samples	Sample volume, mL/ dilution ratio	Added $\mu g\ L^{-1}\ F^-$	Found[a] $\mu g\ L^{-1}\ F^-$	RSD %	Recovery %	Added $\mu g\ L^{-1}\ F^-$	Found[a] $\mu g\ L^{-1}\ F^-$	RSD %	Recovery %	Student's t-test[b]	Variance ratio, F-test[b]
Beverages with and without alcohol											
Orange juice	5/1 : 25	—	18.2 ± 0.8	4.4	—	—	17.5 ± 0.6	3.4	—	1.57	1.8
		25	42.7 ± 1.3	3.0	98.0	25	41.8 ± 1.2	2.9	97.2	—	—
Cherry juice	5/1 : 25	—	17.9 ± 0.8	4.5	—	—	18.7 ± 0.7	3.7	—	1.69	1.3
		25	42.6 ± 1.2	2.8	98.8	25	43.3 ± 1.3	3.0	98.4	—	—
Peach juice	5/1 : 25	—	28.4 ± 1.0	3.5	—	—	27.4 ± 0.9	3.3	—	1.67	1.2
		25	52.6 ± 1.7	3.2	96.8	25	51.7 ± 1.5	2.9	97.2	—	—
Mixed fruit juice	5/1 : 25	—	29.2 ± 1.2	4.1	—	—	29.8 ± 1.0	3.4	—	0.86	1.4
		20	48.2 ± 1.0	3.4	95.0	20	49.0 ± 1.2	2.4	96.0	—	—
Pear juice	5/1 : 25	—	15.3 ± 0.6	3.9	—	—	14.7 ± 0.5	3.4	—	1.72	1.4
		20	34.7 ± 0.7	2.6	97.0	20	34.4 ± 0.8	2.3	98.5	—	—
Lemonade	5/1 : 50	—	10.2 ± 0.4	3.9	—	—	10.3 ± 0.4	3.9	—	0.40	1.0
		25	34.5 ± 1.2	3.8	97.2	25	34.7 ± 1.1	3.5	97.6	—	—
Cola	5/1 : 50	—	15.4 ± 0.6	3.9	—	—	14.6 ± 0.5	3.4	—	1.95	1.4
		25	39.5 ± 1.2	3.0	96.4	25	38.6 ± 1.1	2.8	96.0	—	—
Mandarin juice	5/1 : 50	—	10.7 ± 0.5	4.7	—	—	10.3 ± 0.4	3.9	—	1.40	1.6
		25	34.4 ± 1.2	3.5	95.0	25	34.8 ± 1.2	3.4	98.0	—	—
Plain soda	5/1 : 100	—	10.6 ± 0.4	3.8	—	—	11.0 ± 0.4	3.6	—	1.58	1.0
		25	34.5 ± 1.2	3.5	95.6	25	35.5 ± 1.2	3.4	98.0	—	—
Red wine	5/1 : 50	—	15.2 ± 0.6	3.9	—	—	14.9 ± 0.5	3.4	—	0.86	1.4
		25	40.0 ± 1.4	3.5	99.2	25	39.5 ± 1.5	3.8	98.4	—	—
White wine	5/1 : 50	—	16.8 ± 0.6	3.6	—	—	17.4 ± 0.6	3.4	—	1.58	1.0
		25	40.6 ± 1.4	3.5	95.2	25	41.5 ± 1.5	3.8	96.4	—	—
Beer	5/1 : 100	—	15.4 ± 0.6	3.9	—	—	16.1 ± 0.6	3.7	—	1.85	1.0
		25	40.0 ± 1.4	3.5	98.4	25	40.5 ± 1.3	3.2	97.6	—	—
Soup mix samples											
Tomato soup	5/1 : 25	—	23.8 ± 1.0	4.0	—	—	23.5 ± 0.9	3.8	—	0.50	1.2
		25	49.3 ± 1.6	3.2	102.0	25	49.1 ± 1.5	3.1	102.4	—	—
Spring soup	5/1 : 25	—	14.3 ± 0.6	4.2	—	—	13.8 ± 0.5	3.6	—	1.43	1.4
		25	38.7 ± 1.4	3.5	97.6	25	37.8 ± 1.5	3.8	97.2	—	—
Chicken soup	5/1 : 25	—	28.1 ± 1.2	4.3	—	—	27.4 ± 1.1	4.0	—	0.96	1.2
		25	52.7 ± 1.4	3.5	98.4	25	51.8 ± 1.5	3.8	97.6	—	—
Lentil soup	5/1 : 50	—	20.7 ± 0.7	3.4	—	—	21.4 ± 0.7	3.3	—	1.58	1.0
		25	45.2 ± 1.2	2.7	98.0	25	45.7 ± 1.2	2.6	97.2	—	—
Chicken bouillon	5/1 : 50	—	20.1 ± 0.8	4.0	—	—	19.4 ± 0.7	3.6	—	1.47	1.3
		25	44.6 ± 1.4	3.1	98.0	25	43.5 ± 1.3	3.0	96.4	—	—
Baby food samples											
Mixed baby food	5/1 : 50	—	19.9 ± 0.7	3.5	—	—	21.3 ± 0.5	3.4	—	1.04	1.9
		25	44.3 ± 1.4	3.2	97.2	25	45.5 ± 1.3	2.9	96.8	—	—
Vegetable baby food	5/1 : 50	—	32.4 ± 1.2	3.7	—	—	31.7 ± 1.1	3.5	—	0.96	1.2
		25	57.0 ± 1.7	3.0	98.4	25	56.2 ± 1.6	2.8	98.0	—	—
Apple and peach baby food	5/1 : 50	—	23.1 ± 0.8	3.5	—	—	23.7 ± 0.8	3.4	—	1.19	1.0

Table 4 (*Contd.*)

Samples	After microwave-assisted digestion (n: 5)					After ultrasonic-assisted digestion (n: 5)					
	Sample volume, mL/ dilution ratio	Added $\mu g\ L^{-1}\ F^-$	Found[a] $\mu g\ L^{-1}\ F^-$	RSD %	Recovery %	Added $\mu g\ L^{-1}\ F^-$	Found[a] $\mu g\ L^{-1}\ F^-$	RSD %	Recovery %	Student's *t*-test[b]	Variance ratio, *F*-test[b]
	25		47.5 ± 1.5	3.2	97.6	25	47.8 ± 1.4	2.9	96.4	—	—

[a] The average plus standard deviation of five replicate measurements of total acid hydrolyzed fluoride after pretreatment with two different dissolution approaches. [b] To compare two mean values for independent two-sample *t*- and *F*-tests with equal sample size, the *t*- and *F*-critical values at 95% confidence level and 8 degrees of freedom are 2.31 and 6.39, respectively.

assisted digestion are quantitatively in agreement with those of found after ultrasonic-assisted digestion in terms of accuracy and reliability with the RSD < 5.3%.

5. Comparison of proposed method with methods previously published in the literature

A sensitivity improvement was achieved when compared to previously reported works using UV-Vis detection techniques including MIC-IC (0.03 $\mu g\ g^{-1}$ with RSD of ≤11%),[8] CZE (0.15 $\mu g\ g^{-1}$),[9] CPI-MIP-OES (3–6 $\mu g\ g^{-1}$),[11] HR-CS-MAS (1.0 $mg\ L^{-1}$),[12] ICP-OES (1.4 $mg\ L^{-1}$),[14] TXRF (5 $mg\ L^{-1}$ with RSD of 2.5–8.9%),[16] ET-AAS (14 $\mu g\ L^{-1}$ with RSD of 5–10%),[18] SPE-spectrophotometry (15 $\mu g\ L^{-1}$),[35] LLE-ETV-GF-MAS (10 $\mu g\ L^{-1}$),[36] HS-SDME-IC (3.8 $\mu g\ L^{-1}$),[37] HR-CS-GF-MAS (0.38 $mg\ L^{-1}$),[38] HS-SPME-GC-FID (6 $\mu g\ L^{-1}$ with RSD of ≤5.45–11.94%),[39] HS-SDME-GC-FID (4.4 $\mu g\ L^{-1}$ with RSD of ≤5.41%),[40] potentiometry after microwave-assisted digestion (1.8 $\mu g\ L^{-1}$ with poor precision in a range of 1–8%),[7] ISE (340 $\mu g\ L^{-1}$)[41] and FI-ISE (340 $\mu g\ L^{-1}$)[42] with and without preconcentration using different analytical methods in terms of detection limits (LODs). The LOD (1.45 $\mu g\ L^{-1}$), preconcentration factor (PF) (62.5), and sensitivity enhancement factor (EF) (86.6) obtained in this study are generally either better than or comparable to those of the reported detection methods. Also, it has relatively a wider working range of 5–360 $\mu g\ L^{-1}$ and RSD < 4.5% (as a measure of precision) at low fluoride concentrations in complex matrices such as beverages and foods. The more sensitive detection techniques such as HR-CS-GF-MAS based on the molecular absorption of GaF with a detection limit of 0.26 $\mu g\ L^{-1}$ with and without preconcentration with SPME[43,44] are generally time-consuming, expensive, relatively less precise and instrumentation typically requires experienced users. As a result, the developed micellar-sensitive method provides advantages of greater linear range, low detection limit, high selectivity, good precision, adequate accuracy, quantitative recovery, and comparable preconcentration factors for the spectrophotometric monitoring of trace fluoride in selected real samples. Using a volume of 50 mL, one sample can be analyzed by means of CPE–UV-Vis after fast and efficient digestion of samples under ultrasonic and microwave effect in a short time.

6. Conclusions

In this study, a new CPE–UV-Vis method was described to be a rapid, accurate and reliable analytical technique for determination of total acid hydrolyzed fluoride in selected foods/beverages. The method allowed fluoride determination at 1.45 $\mu g\ L^{-1}$ levels in a wide linear range of 5–360 $\mu g\ L^{-1}$ at 638 nm, thus representing a promising approach for monitoring fluoride in samples. This low-cost and versatile tool presents several additional advantages such as wide linear range, low detection limit, adequate accuracy, quantitative recovery, and high preconcentration and sensitivity enhancement factors, which could be available in nearly every research laboratory. In

addition, the CPE approach, which is efficiently used in the method for separation and preconcentration, is also low cost, easy to use, simple, fast, safe and non-polluting. Consequently, the developed analytical method may be considered as an alternative to sensitive, expensive, time-consuming complex analytical techniques that require experienced users such as MIP-AES, GF-EV-MAS, TXRF and ETV-ICP-MS.

Disclosures

The authors declare that they have no conflicts of interest. This article does not contain any procedures using human or animal subjects.

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