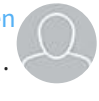
Evaluation of different SIA sample–buffer configurations using a fluoride-selective membrane electrode as detector

ARTICLE *in* TALANTA · JUNE 2000

Impact Factor: 3.55 · DOI: 10.1016/S0039-9140(99)00359-8 · Source: PubMed

3 AUTHORS:

Jacobus (Koos) FREDERICK Van Staden
Institutul National De Cercetare – De…
303 PUBLICATIONS **3,493** CITATIONS
SEE PROFILE



Raluca-Ioana Stefan
National Institute of Electrochemistr…
196 PUBLICATIONS **2,080** CITATIONS
SEE PROFILE

Sema Birghila
Universitatea Ovidius Constanţa
15 PUBLICATIONS **64** CITATIONS
SEE PROFILE

ELSEVIER

Talanta 52 (2000) 3–11

Talanta

www.elsevier.com/locate/talanta

Evaluation of different SIA sample–buffer configurations using a fluoride-selective membrane electrode as detector☆

Jacobus (Koos) F. van Staden *, Raluca-Ioana Stefan, Semaghiul Birghila

Department of Chemistry, University of Pretoria. Pretoria 0002, South Africa

Received 21 July 1999; received in revised form 7 December 1999; accepted 8 December 1999

Abstract

The peak profiles of four different buffer–sample SIA configurations, e.g. buffer–sample; sample–buffer; buffer–sample–buffer and sample–buffer–sample with the last two in the sandwich mode were evaluated with a fluoride-selective membrane electrode as detector. The best response characteristics and peak shapes as well as recovery and precision values were obtained for the buffer–sample configuration. For low concentration levels, sandwich SIA configurations are more suitable, when optimum buffer and pH are used. The utilisation of a cheap electrolyte with a minimum consumption of buffer and a cheap, robust instrumentation made the SIA system suitable for on-line determination of fluoride.

1. Introduction

Recently, the fluoridation of water become increasingly important. The influence of the fluoridated water on dental fluorosis and dental caries was intensively studied [1–5]. It must also be taken into account that the maximum level of the fluoride in water should be 1.500 μg l^{-1} [6]. At the same time, the fluoride content contributes to the quality of toothpaste. In order to sustain the quality of life and for healthy reasons, the fluoride content in water and toothpaste should be controlled carefully. The fluoride-selective, membrane electrode is an ideal detector for direct determination of fluoride in water and toothpaste. The reliability of the response characteristics made it suitable to be used as detector in FIA [7,8] and SIA [9] systems.

Sequential injection analysis (SIA), launched in 1990 [10,11] is a technique that has a tremendous potential especially for on-line process measurements and in the monitoring of the environment, due to the simplicity and convenience with which sample manipulations can be automated. The versatility of the technique is centred around a selection valve where each port of the valve allows a different operation to be performed [10,11]. The basic components of the system are a peristaltic pump with only one carrier stream, a single selection valve, a single channel and a detector. The

☆ Presented at The Tenth International Conference on Flow Injection Analysis, June 20–25, 1999, Prague, Czech Republic.

* Corresponding author. Tel: +27-12-4202515; fax: +27-12-3625297.

E-mail address: koos.vanstaden@chem.up.ac.za (J.F. van Staden)

0039-9140/00/$ - see front matter
PII: S0039-9140(99)00359-8

concept is based on the sequential injection of a wash solution, sample zone and reaction zone(s) into a channel [12–14]. In this way a stack of well-defined zones adjacent to each other is obtained in a holding coil. After the valve has been selected to the detector position, the flow in the carrier stream is reversed and the zones mutually disperse and penetrate each other as they passed through a reaction coil to the detector. The flow reversal as a result of the injection step therefore creates a composite zone in which the sample and reagent zone penetrate each other due to combined axial and radial dispersion. Operational parameters affecting zone penetration has been studied and defined [13–15]. The authors [13–15] showed that the order in which the zones are stack in the holding coil depends upon the type of chemistry being utilised. The advantages of SIA have been discussed in detail by Růžička and Gűbeli [12] and in comprehensive reviews [16–18]. Although the sample throughput frequency of an SIA system is normally less than that of the conventional FIA system [12,13], the major advantage of SIA is the more cost-effective use of reagents.

This paper presents the evaluation of the peak profiles of four different buffer–sample SIA configurations with a fluoride-selective, membrane electrode and the application to the determination of fluoride in tap water and toothpaste.

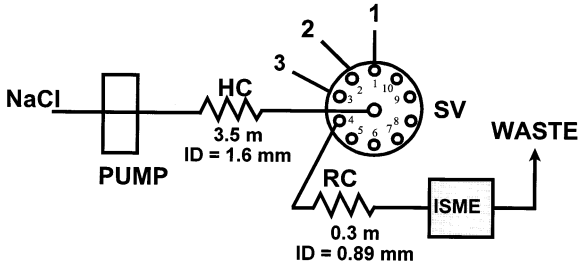


Fig. 1. Sequential analysis systems design. Buffer–sample (BS): 1, buffer; 2, sample; 3, detector. Sample–buffer (SB): 1, sample; 2, buffer; 3, detector. Buffer–sample–buffer (BSB): 1, buffer; 2, sample; 3, buffer; 4, detector. Sample–buffer–sample (SBS): 1, sample; 2, buffer; 3, sample; 4, detector.

2. Experimental

2.1. Reagents and solutions

All reagents were prepared from analytical reagent grade chemicals unless specific otherwise.

De-ionised water from a Modulab system (Continental Water Systems, San Antonio, TX) was used to prepare all aqueous solutions and dilutions.

2.1.1. Fluoride stock solution

A 10^{-1} mol l^{-1} fluoride stock solution was prepared by dissolving 4.2 g NaF in 1 l of de-ionised water. Working solutions are obtained by serial dilution of the stock solution.

2.1.2. TISAB II buffer solution

Fifty seven millilitres glacial acetic acid and 58.5 g dried NaCl were dissolved in 500 ml distilled water. The pH was adjusted to 5.5 using a 5 mol l^{-1} NaOH solution. The solution was quantitatively diluted to mark in a 1 l volumetric flask with de-ionised water.

2.1.3. Phosphate buffer solution

A solution containing 71.64 g l^{-1} $Na_2HPO_4 \cdot 12$ H_2O and 27.60 g l^{-1} $NaH_2PO_4 \cdot H_2O$ in de-ionised water was used as buffer solution.

2.1.4. NaCl solution

A 1 mol l^{-1} NaCl was used as carrier stream. The solution was obtained by dissolving 58.5 g dried NaCl in 1 l de-ionised water.

2.1.5. Preparation of toothpaste samples

Five-gram samples (Aquafresh toothpaste) were weighted into a 100 ml beaker. Five millilitres de-ionised water and 5 ml concentrated HCl were added to the sample and homogenised. Buffered with TISAB II (1:1 (v/v)) the beaker was inserted into a water bath at 90°C for 1 min. After cooling the content of the beaker was transferred to a 1000 ml volumetric flask and filled to the mark with de-ionised water.

Table 1
Device sequence for one cycle of the fluoride selective, membrane electrode–SIA system, buffer–sample (BS)

Time (s)	Pump	Valve	Description
0	Off	Buffer	Pump off, select buffer stream (valve position 1)
5.0	Reverse		Draw up buffer solution
8.50	Off	Sample	Pump off, select sample stream (valve position 2)
10.50	Reverse		Draw up sample solution
15.00	Off		Pump stop
16.00		Detector	Select detector (valve position 3)
17.00	Forward		Pump buffer and sample zones to detector
120.00	Off	Home	Pump off, return to starting position (valve position 1)

Table 2
Device sequence for one cycle of the fluoride selective, membrane electrode–SIA system sample–buffer (SB)

Time (s)	Pump	Valve	Description
0	Off	Sample	Pump off, select sample stream (valve position 1)
5.0	Reverse		Draw up sample solution
9.5	Off	Buffer	Pump off, select buffer stream (valve position 2)
11.50	Reverse		Draw up buffer solution
14.80	Off		Pump stop
15.80		Detector	Select detector line (valve position 3)
16.80	Forward		Pump buffer and sample zones to detector
120.00	Off	Home	Pump off, return valve to starting position (valve position 1)

2.2. Apparatus

The sequential injection system (SIA) is illustrated in Fig. 1. It was constructed from:

1. A Gilson Minipuls peristaltic pump;
2. A ten-port electrically actuated selection valve (Model ECSD10P, Valco Instruments, Houston, Texas);
3. An Orion fluoride-selective, membrane electrode (Orion Research Incorporated Laboratory products Group) Model 94-09 was used for all measurements in combination with a double junction reference Orion electrode Model 90-02 connected to an Orion Research Microprocessor Ionalyzer (Model 901).

Data acquisition and device control were achieved using a PC 30-B interface board (Eagle Electric, Cape Town, South Africa). The FLOWTEK software package (obtainable from Mintek) was used throughout for device control and data acquisition [19]. Tygon tubings were used for the holding (HC) and reaction coils (RC).

2.3. Description of the SIA configurations

Device sequences for one cycle of a sequential injection system for each of the different sample–buffer configurations are outlined as follows: buffer–sample (BS) (Table 1); sample–buffer (SB) (Table 2); buffer–sample–buffer (BSB) (Table 3); sample–buffer–sample (SBS) (Table 4).

3. Results and discussion

3.1. Optimisation

It was necessary to optimise a number of physical and chemical parameters to obtain the highest sensitivity and precision. The original optimisation was done using the configuration where the aspiration order into the SIA holding coil was buffer–sample (BS). The optimum conditions were applied to all the other configurations.

Table 3
Device sequence for one cycle of the fluoride selective, membrane electrode–SIA system, buffer–sample–buffer (BSB)

Time (s)	Pump	Valve	Description
0	Off	Buffer	Pump off, select buffer stream (valve position 1)
5	Reverse		Draw up buffer solution
8.3	Off	Sample	Pump off, select sample stream (valve position 2)
10.30	Reverse		Draw up sample solution
14.80	Off	Buffer	Pump off, select buffer stream (valve position 3)
16.80	Reverse		Draw up buffer solution
20.10	Off		Pump stop
21.10		Detector	Select detector (valve position 4)
22.10	Forward		Pump buffers and sample zones to detector
118	Off	Home	Pump off, return to starting position (valve position 1)

Table 4
Device sequence for one cycle of the fluoride selective, membrane electrode–SIA system, sample–buffer–sample (SBS)

Time (s)	Pump	Valve	Description
0	Off	Sample	Pump off, select sample stream (valve position 1)
5	Reverse		Draw up sample solution
9.50	Off	Buffer	Pump off, select buffer stream (valve position 2)
11.50	Reverse		Draw up buffer solution
16.50	Off	Sample	Pump off, select sample stream (valve position 3)
18.50	Reverse		Draw up sample solution
20.50	Off		Pump stop
21.50		Detector	Select detector (valve position 4)
22.50	Forward		Pump buffer and sample zones to detector
118	Off	Home	Pump off, return to starting position (valve position 1)

3.1.1. Flow rate

The influence of the flow rate on sensitivity and precision was evaluated and the results are illustrated in Fig. 2. A total sample volume of 270 μl was used during these evaluations. The volume was adjusted to remain constant for every flow rate studied. This resulted in longer times for lower flow rates and shorter times for higher flow rates. The optimum flow rate was chosen to be 3.61 ml min^{-1}.

3.1.2. Sample volume

It is important to optimise this parameter to ensure that effective mixing with the buffer solutions was obtained. Different sample volumes were investigated and the results are summarised in Table 5. A sample volume of 270 μl (R.S.D. = 0.14%) was selected for optimum working conditions.

3.1.3. Buffer volume

Different volumes of TISAB buffer solution were aspirated into the SIA system to evaluate the volume of the buffer solution. Fig. 3 illustrated that the optimum volume is 300 μl (R.S.D. = 0.31%).

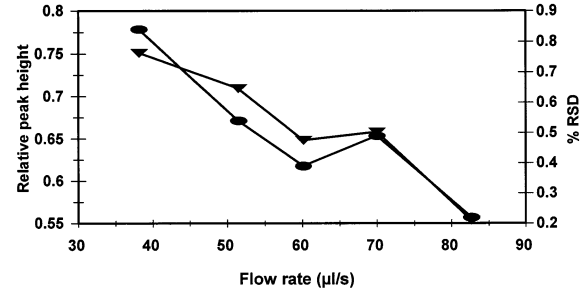


Fig. 2. Optimisation of flow rate. (▲) Relative peak height; (●) %R.S.D.

Table 5
Effect of sample volume on sensitivity and precision

Volume (μl)	200	220	250	270	300	350
Mean relative peak height	0.7831	0.8131	0.8371	0.8390	0.8449	0.8849
R.S.D.%	0.24	0.37	0.27	0.14	0.28	0.37

3.1.4. Diameter and length of tubing

3.1.4.1. Holding coil. The holding coil serves as a holding reservoir, which prevents the stack of zones from entering the conduit of the pumping tube in the peristaltic pump where deformation could take place. The length and diameter of the holding coil did not have a large influence and a 3.5 m (1.6 mm i.d.) Tygon tubing coil gave was used.

3.1.4.2. Reaction coil. The length (Fig. 4) and diameter (Fig. 5) of the reaction coil were optimised using different lengths and diameters of Tygon tubings. As it is shown in the figures, the optimum length and diameter for the reaction coil were found to be 0.3 m and 0.89 i.d., respectively.

3.2. Response characteristics of the fluoride-selective, membrane electrode in SIA systems

The response characteristics of the fluoride-selective membrane electrode were evaluated for the different proposed SIA configurations with TISAB II (pH 5.5) and phosphate (pH 5.5; 6.6; 7.6) as individual buffers. As is shown in Table 6, the best detection limit (2.03 μg l^{-1}) was obtained for the BS SIA system (TISAB II, pH 5.5). The largest working concentration ranges were obtained for BS (TISAB II, pH 5.5) and SBS (TISAB II, pH 5.5 and phosphate, pH 6.6).

The coefficients for the equation of calibration:

$$H = H^0 + S\mathrm{pF}$$

where $\mathrm{pF} = -\log c_F$ are given in Table 6. The values for correlation coefficients are larger than 0.9900, which are still good enough.

As the concentration level of fluoride in drinking water is normally very low, and difficult to be determined, it was also important to evaluate the different SIA configurations separately for the determination of low concentrations of fluoride.

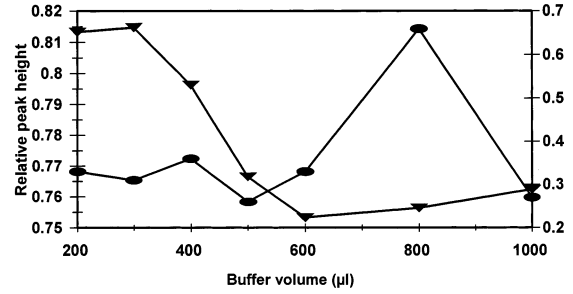


Fig. 3. Optimisation of the buffer volume. (▲) Relative peak height; (●) %R.S.D.

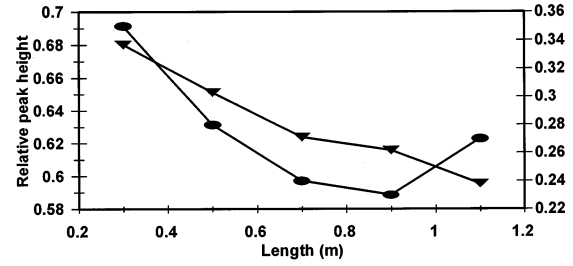


Fig. 4. Optimisation of reaction coil length. (▲) Relative peak height; (●) %R.S.D.

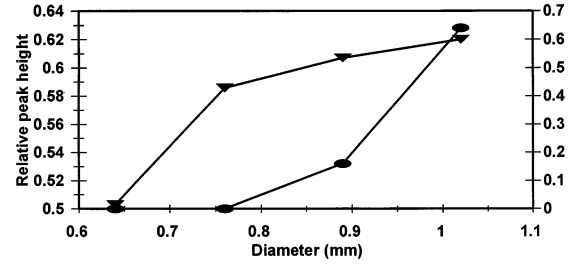


Fig. 5. Optimisation of reaction coil diameter. (▲) Relative peak height; (●) %R.S.D.

Table 6
Response characteristics of the fluoride selective membrane electrode in different SIA configurations

pH	Method	H^0	S	r	Working concentration range (mol l^{-1})	Detection limit (mol l^{-1})
5.5 (TISAB II)	SB	2.00	−0.44	0.9992	10^{-5}–10^{-1}	3×10^{-5}
	BS	2.11	−0.43	0.9999	5×10^{-6}–10^{-1}	1.07×10^{-7}
	SBS	2.20	−0.50	0.9962	5×10^{-6}–10^{-1}	6.08×10^{-6}
	BSB	2.06	−0.45	0.9980	10^{-5}–10^{-1}	2×10^{-6}
5.5 (phosphate)	SB	2.11	−0.56	0.9999	5×10^{-4}–10^{-1}	1.75×10^{-4}
	BS	2.05	−0.47	0.9969	10^{-4}–10^{-1}	5×10^{-5}
	SBS	2.12	−0.52	0.9999	10^{-4}–10^{-1}	8×10^{-5}
	BSB	1.94	−0.52	0.9994	5×10^{-4}–10^{-1}	1.8×10^{-4}
6.6 (phosphate)	SB	0.80	−0.20	0.9900	10^{-4}–10^{-1}	9.5×10^{-5}
	BS	2.04	−0.46	0.9990	5×10^{-5}–10^{-1}	3.6×10^{-5}
	SBS	2.00	−0.45	0.9956	5×10^{-6}–10^{-1}	3.5×10^{-6}
	BSB	1.99	−0.53	0.9997	5×10^{-4}–10^{-1}	1.76×10^{-4}
7.6 (phosphate)	SB	1.70	−0.47	0.9999	10^{-3}–10^{-1}	2.3×10^{-4}
	BS	1.90	−0.45	0.9999	5×10^{-5}–10^{-1}	3.6×10^{-5}
	SBS	1.95	−0.45	0.9999	5×10^{-5}–10^{-1}	2.4×10^{-5}
	BSB	1.77	−0.45	0.9999	10^{-4}–10^{-1}	5.2×10^{-5}

Table 7
Response characteristics of the fluoride selective membrane electrode in different SIA configurations at low concentration levels

pH	Method	H^0	S	r	Working concentration range (mol l^{-1})	Detection limit (mol l^{-1})
5.5 (TISAB II)	SB[a]	–	–	–	–	–
	BS[a]	–	–	–	–	–
	SBS	2.55	−0.32	0.9892	10^{-8}–10^{-6}	8.5×10^{-9}
	BSB	0.35	−0.03	0.9266	10^{-10}–10^{-6}	1.7×10^{-12}
5.5 (phosphate)	SB[a]	–	–	–	–	–
	BS	0.79	−0.11	0.9972	10^{-7}–5×10^{-5}	9×10^{-8}
	SBS[a]	–	–	–	–	–
	BSB[a]	–	–	–	–	–
6.6 (phosphate)	SB[a]	–	–	–	–	–
	BS	0.04	−0.04	0.9779	10^{-8}–10^{-5}	10^{-9}
	SBS	−0.70	−0.14	0.9773	5×10^{-8}–8×10^{-6}	10^{-8}
	BSB[a]	–	–	–	–	–
7.6 (phosphate)	SB	−0.27	−0.06	0.9995	10^{-8}–5.5×10^{-5}	5×10^{-9}
	BS	−0.24	−0.08	0.9630	5×10^{-7}–10^{-5}	10^{-7}
	SBS[a]	–	–	–	–	–
	BSB	−0.13	−0.03	0.9992	10^{-8}–2×10^{-5}	5×10^{-9}

[a] For these methods no response was recorded at low concentration level.

The calibration was repeated for low concentration levels, using each SIA system. The results are shown in Table 7.

There are a few configurations that can be used for the determination of low concentration levels of fluoride. In this regard, the best working concentration ranges (10^{-8}–10^{-6} mol l^{-1}) and detection limits (10^{-10}–10^{-6} mol l^{-1} are given by sandwiches SBS and BSB (TISAB II, pH 5.5).

If we summarised the results shown in both Tables 6 and 7, and also in Fig. 6, the best results are obtained using TISAB II (pH 5.5) with a BS

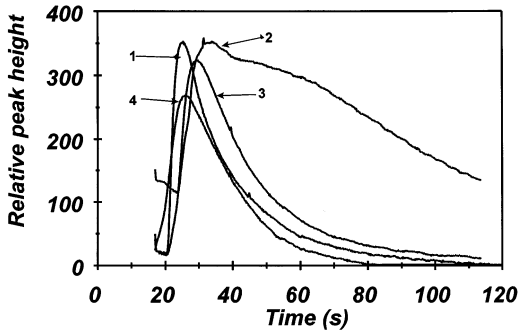


Fig. 6. The shape of the peaks for 1, BS; 2, SBS; 3, BSB; and 4, SB SIA systems when TISAB II was used.

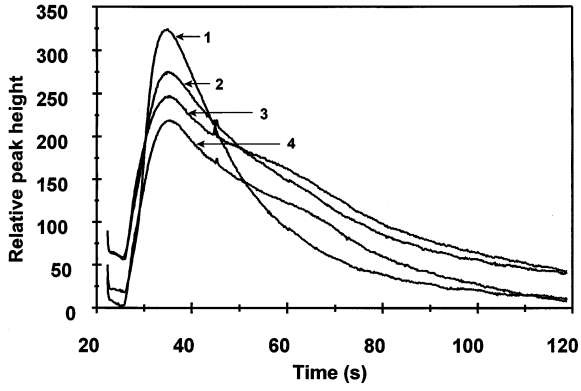


Fig. 7. The influence of buffer and pH for SB SIA system. 1, TISAB II; 2, phosphate buffer pH 5.5; 3, phosphate buffer pH 6.6; 4, phosphate buffer pH 7.6.

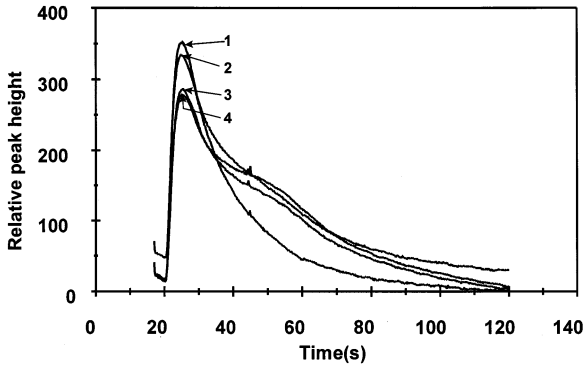


Fig. 8. The influence of buffer and pH for BS SIA system. 1, TISAB II; 2, phosphate buffer pH 5.5; 3, phosphate buffer pH 6.6; 4, phosphate buffer pH 7.6.

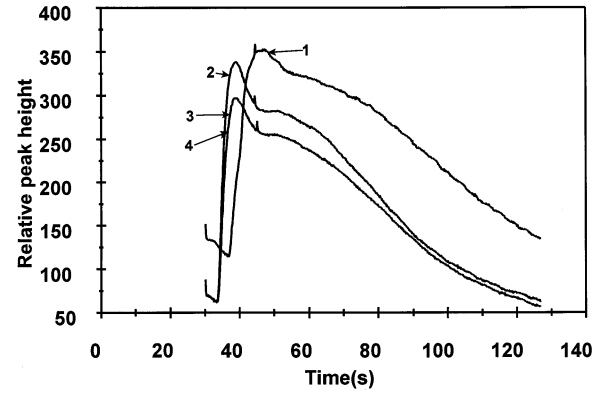


Fig. 9. The influence of buffer and pH for SBS SIA system. 1, TISAB II; 2, phosphate buffer pH 5.5; 3, phosphate buffer pH 6.6; 4, phosphate buffer pH 7.6.

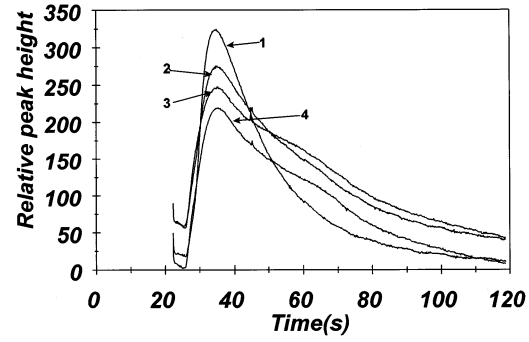


Fig. 10. The influence of buffer and pH for BSB SIA system. 1, TISAB II; 2, phosphate buffer pH 5.5; 3, phosphate buffer pH 6.6; 4, phosphate buffer pH 7.6.

SIA configuration. For low concentration levels sandwiches are recommended.

3.3. The dependence of the fluoride-selective, membrane electrode response on pH and buffer type

The dependence of the fluoride selective, membrane electrode on the buffer type and pH was evaluated using TISAB II (pH 5.5) and phosphate (pH 5.5; 6.6; 7.6) buffers. The results are shown in Figs. 7–10. The largest and best shape peaks were obtained for all the studied SIA configurations when TISAB II (pH 5.5) was used. The dependence of the response characteristics on pH and buffer type is also quantified in Tables 6 and 7. As

Table 8
Peak heights obtained for different pH values and buffers

pH	BS	SB	BSB	SBS
5.5 (TISAB II)	0.8813	0.6828	0.8179	0.7031
5.5 (phosphate)	0.6014	0.4253	0.3979	0.5639
6.6 (phosphate)	0.6345	0.2002	0.4076	0.5835
7.6 (phosphate)	0.5566	0.3271	0.4602	0.6042

also seen from Table 8 the optimum pH — in terms of peak height — is 5.5 (TISAB II). The R.S.D. values obtained for all methods are around 3×10^{-3}% (No significant differences of R.S.D. values were recorded for various pH and methods utilised.).

3.4. Selectivity of fluoride membrane electrode

The selectivity was studied using the mixed solutions method. The effects of some possible mutual interferences on the response of the electrode as well as possible interferences from other anions were studied. Table 9 shows that the response of the fluoride-selective, membrane electrode was not affected by the presence of Cl^-, Br^- I^- and CO_3^{2-} ions even when the ratio between the concentration of fluoride and interfering ions (mol) was 1:1000. This fact demonstrates the specificity of the electrode for the primary ion and that the electrodes could be used in sequential systems.

3.5. Analytical applications

The high selectivity and sensitivity obtained by the fluoride-selective membrane electrode in SIA systems made it suitable to be used for the assay of fluoride in tap water and toothpaste samples. As is shown in Table 10 for low concentration levels sandwich SIA systems (TISAB II, pH 5.5) are the most reliable. When phosphate is used as buffer, the SB SIA system can also be used with high reliability for low concentration levels of fluoride assay in the tap water (Table 10).

All the proposed SIA systems can be used reliably for the assay of fluoride in toothpaste (Table 11). The best recovery of fluoride in toothpaste was recorded when TISAB II (pH 5.5) was used (99.60%).

4. Conclusions

The peak profiles of four different buffer–sample SIA configurations, e.g. buffer–sample; sam-

Table 9
Selectivity coefficients of the fluoride selective membrane electrode

pH	Method	$pK^{pot}_{F^-,\ Cl^-}$	$pK^{pot}_{F^-,\ Br^-}$	$pK^{pot}_{F^-,\ I^-}$	$pK^{pot}_{F^-,\ CO_3^{2-}}$
5.5 (TISAB II)	SB	3.03	3.02	3.03	4.03
	BS	3.05	3.06	3.04	4.04
	SBS	3.30	3.01	3.04	4.05
	BSB	3.04	3.03	3.02	4.03
5.5 (phosphate)	SB	3.12	3.11	3.49	4.4
	BS	3.03	3.04	3.03	4.04
	SBS	3.08	3.05	3.03	4.05
	BSB	3.10	3.50	3.08	4.09
6.6 (phosphate)	SB	3.0	3.01	3.00	4.08
	BS	3.06	3.09	3.06	4.04
	SBS	3.08	3.06	3.03	4.04
	BSB	3.5	3.12	3.12	4.40
7.6 (phosphate)	SB	3.47	3.23	3.10	4.22
	BS	3.20	3.18	3.16	4.22
	SBS	3.35	3.28	3.24	4.29
	BSB	3.19	3.16	3.14	4.17

Table 10
Determination of fluoride in water samples

pH	Method	Recovery[a] (%)
5.5 (TISAB II)	SB	98.57 ± 0.008[b]
	BS	99.20 ± 0.001[b]
	SBS	98.77 ± 0.002
	BSB	99.97 ± 0.001
5.5 (phosphate)	SB	96.40 ± 0.007[b]
	BS	95.49 ± 0.002
	SBS	95.50 ± 0.005[b]
	BSB	95.60 ± 0.004[b]
6.6 (phosphate)	SB	98.67 ± 0.008[b]
	BS	98.77 ± 0.003
	SBS	99.49 ± 0.004
	BSB	98.50 ± 0.002[b]
7.6 (phosphate)	SB	101.60 ± 0.009
	BS	96.32 ± 0.002
	SBS	98.20 ± 0.004[b]
	BSB	97.01 ± 0.003

[a] All results are the average of ten determinations for the same concentration of fluoride in water (5×10^{-7} mol l^{-1}).
[b] Addition standard method was used for fluoride assay.

Table 11
Determination of fluoride in toothpaste

pH	Method	Recovery[a] (%)
5.5 (TISAB)	SB	99.74 ± 0.007
	BS	98.93 ± 0.002
	SBS	99.68 ± 0.003
	BSB	99.96 ± 0.001
5.5 (phosphate)	SB	103.80 ± 0.009
	BS	94.53 ± 0.002
	SBS	97.37 ± 0.004
	BSB	90.00 ± 0.008
6.6 (phosphate)	SB	82.03 ± 0.009
	BS	92.22 ± 0.002
	SBS	100.32 ± 0.003
	BSB	96.70 ± 0.004
7.6 (phosphate)	SB	98.94 ± 0.008
	BS	99.20 ± 0.007
	SBS	99.99 ± 0.001
	BSB	98.93 ± 0.002

[a] All results are the average of ten determinations.

ple–buffer; buffer–sample–buffer and sample–buffer–sample with the last two in the sandwich mode were evaluated with a fluoride-selective membrane electrode as detector. The best response characteristics and peak shapes as well as recovery and precision values were obtained for the buffer–sample configuration.

For low concentration levels, sandwich SIA configurations are more suitable, when optimum buffer and pH are used. The utilisation of a cheap electrolyte with a minimum consumption of buffer and a cheap, robust instrumentation made the SIA system suitable for on-line determination of fluoride.

References

[1] P. Levallois, J. Grondin, S. Gingras, Rev. Can. Sante Publique 89 (1998) 162.
[2] J.M. Broseur, M. Payette, C. Bedos, Rev. Can. Sante Publique 89 (1998) 274.
[3] J.P. Loyola-Rodriguez, A.J. Pozos-Guillen, J.C. Hernandez-Guerrrero, Salud Publica Mexico 40 (1998) 438.
[4] A.J. Spencer, Aust. New Zealand J. Public Health 22 (1998) 149.
[5] J.V. Kumar, P.A. Swango, L.L. Lininger, G.S. Leske, E.L. Green, V.B. Haley, Am. J. Public Health 88 (1998) 1866.
[6] F.W. Filield, The analysis of water, in: F.W. Fifield, P.J. Haines (Eds.), Environmental Analytical Chemistry, Blackie, Glasgow, 1995.
[7] J.F. van Staden, R.I. Stefan, Talanta 49 (1999) 1017.
[8] R.I. Stefan, J.F. van Staden, Pharm. Helv. Acta 73 (1999) 307.
[9] J. Alpizar, A. Crespi, A. Cladera, R. Forteza, V. Cerda, Electroanalysis 8 (1996) 1051.
[10] J. Růžička, G.D. Marshall, Anal. Chim. Acta 237 (1990) 329.
[11] J. Růžička, G.D. Marshall, G.D. Christian, Anal. Chem. 62 (1990) 1861.
[12] J. Růžička, T. Gűbeli, Anal. Chem. 63 (1991) 1680.
[13] T. Gűbeli, G.D. Christian, J. Růžička, Anal. Chem. 63 (1991) 2407.
[14] D.J. Tucker, B. Toivola, C.H. Pollema, J. Ruzicka, G.D. Christian, Analyst 119 (1994) 975.
[15] G.D. Marshall, J.F. van Staden, Proc. Control Quality 3 (1992) 251.
[16] J. Růžička, Anal. Chim. Acta 261 (1992) 3.
[17] G.D. Christian, J. Růžička, Anal. Chim. Acta 261 (1992) 11.
[18] J. Růžička, Analyst 119 (1994) 1925.
[19] G.D. Marshall, J.F. van Staden, Anal. Instrum. 20 (1992) 79.