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On-line pervaporation separation process for the potentiometric determination of fluoride in "dirty" samples

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Abstract

A selective method for the determination of fluoride in contaminated samples based on pervaporation of a volatile derivative and potentiometric monitoring of the anion after collection in a basic solution has been developed. Fluoride was converted to volatile trimethylfluorosilane by reaction with hexamethyldisilazane, and absorbed in dilute NaOH solution. Both the continuous and stopped-flow modes were used in order to accomplish a variable efficiency of the separation process thus enlarging the determination range which was established between 5 and 100 mg l^{-1}, the precision ranging between 2.60 and 3.58%. The determination of the analyte in samples from different sources (i.e., tap water, well water, fertilizers and ceramic industry wastewater) testifies to its usefulness.

Keywords: Potentiometry; Pervaporation; Fluoride; Dirty samples

1. Introduction

Non-chromatographic continuous separation techniques appear to be a very promising alternative to chromatographic ones, since they can improve both the sensitivity of a method by including preconcentration steps and the selectivity by avoiding matrix effects or particular interferents [1,2].

Membrane-based non-chromatographic continuous separation techniques are especially useful for increasing selectivity; nevertheless, they involve analyte preconcentration in some cases, thus improving sensitivity also. A drawback arising from the use of these techniques is the possible clogging of the membrane pores due to dirty samples or to the presence of components of high molecular weight. This shortcoming is overcome by using pervaporation (which can be defined as a combination of continuous evaporation and gas diffusion), as both the permeating species are selected in terms of vapour pressure, so that components with high molecular weight are rejected by the membrane [3], and because the sample does not come into contact with the membrane. In addition, deterioration of the membrane is avoided. Pervaporation has been used in industry for many years but scarcely on a laboratory scale. Pinzing et al. [4] used a pervaporation unit for the simultaneous determination of ethanol and biacetyl based on an enzymatic derivatization reaction. Recently, a pervaporation module was designed by our research team [5] and its performance was established in terms of its efficiency [6].

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Fluorine is one of the elements the determination of which is subjected most to interference from other species either by precipitation as fluorides or by formation of strong metal–fluoride complexes. For this reason separation of fluoride prior to its determination is commonplace. Separation of fluoride by distillation is time-consuming so new methods are aimed at overcoming the need for it.

A method for the determination of fluoride based on the conversion of fluoride to the volatile trimethylfluorosilane (TMFS) using hexamethyldisilazane (HMDSA) in acidic medium as converting reagent is reported here. TMFS evaporates and diffuses through a hydrophobic membrane to be absorbed into a sodium hydroxide acceptor stream [7,8] at the upper part of the pervaporation module. Fluoride is then determined by a fluoride-selective electrode. The reaction for generation of the volatile compound can be described as follows:

$$2[(CH_3)_3Si]_2NH + 4HF + H_2SO_4 \rightarrow 4(CH_3)_3SiF + (NH_4)_2SO_4$$

The chemical reaction of the absorption of TMFS in the basic solution is:

$$2(CH_3)_3SiF + 2NaOH \rightarrow [(CH_3)_3Si]_2O + NaF + H_2C$$

2. Experimental

2.1. Reagents and solutions

Sodium fluoride (extra pure, Merck) was dried at 130°C for 1 h and 5.528 g of the dried product was

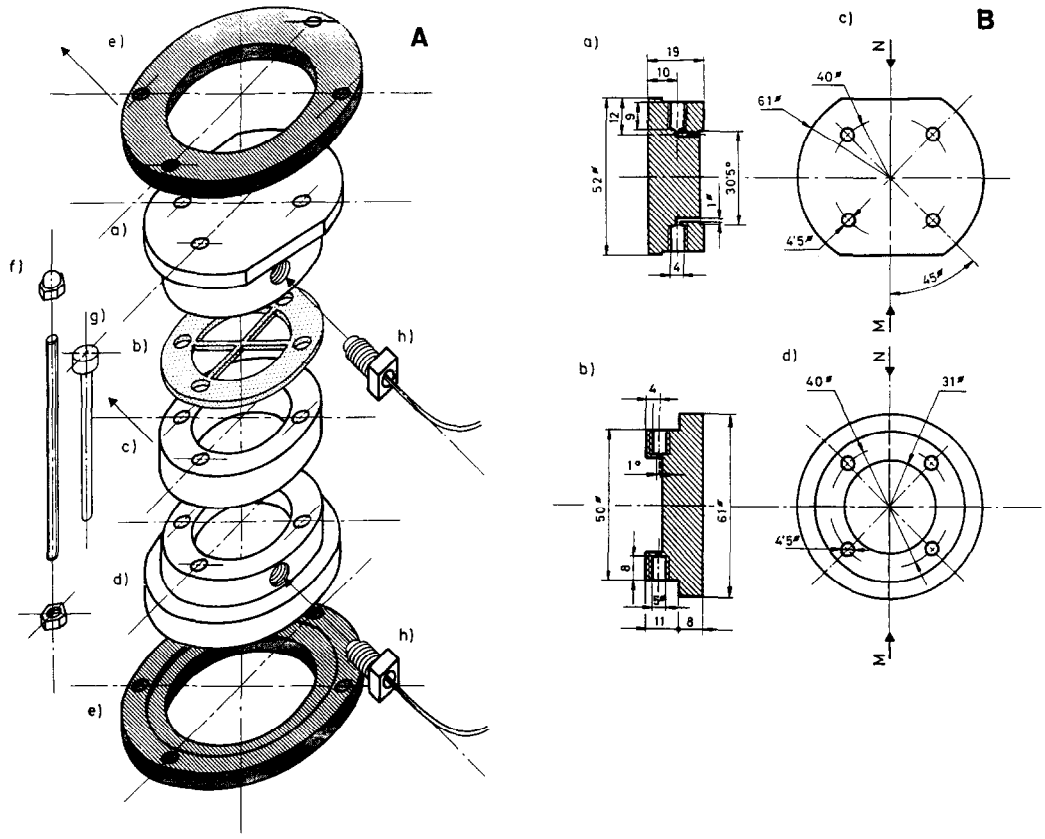

Fig. 1. (A) Parts of the pervaporation module. (a) Receptor chamber, (b) membrane support, (c) spacers, (d) donor/sample chamber, (e) aluminium supports, (f) and (g) rods for screwing and aligning the module, (h) connectors. (B) Cross-sectional (a and b) and plane views (c and d) of the acceptor and sample chambers, respectively.

dissolved in 250 ml of Milli-Q purified water to make a 10 g l^{-1} fluoride stock solution. Standards in the range 5–100 mg l^{-1} were prepared by appropriate dilutions of the stock solution. The 1.5% (v/v) hexamethyldisilazane (HMDSA, Aldrich) solution was prepared daily by measuring out a volume of the acid solution (2 M H_2SO_4) into a flask, adding the appropriate volume of HMDSA and stirring for 5 min. After standing for 15 min, the upper organic layer was aspirated off. The 0.05 M sodium hydroxide solution used as acceptor stream in the pervaporation cell was prepared by dissolving the appropriate amount of NaOH (pro analysi, Merck) in Milli-Q water. Sulphuric acid solutions were prepared by diluting appropriate volumes of the concentrated reagent (96% puriss., Panreac) in Milli-Q water. A 0.2 M acetic acid–0.1 M potassium chloride solution was used in order to keep the pH constant and was prepared by dissolving 37.3 g of KCl (pro analysi, Merck) and 4.4 ml of glacial acetic acid (puriss., Panreac) in 500 ml of Milli-Q water.

Cellulose, polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE) membranes of 5.0 μm pore size and 47-mm diameter purchased from Millipore were also used.

2.2. Instruments and apparatus

Two four-channel Gilson Minipuls-3 peristaltic pumps, fitted with rate selectors, four Rheodyne 5041 injection valves (two of them acting as switching valves), and PTFE tubing of 0.7 mm i.d. were used to build the hydrodynamic manifold. The fluoride-selective electrode (Metrohm 6.0502.150) was fitted in a laboratory-made flow-cell with an inlet and an outlet connector and a channel going through the middle of it to provide contact of the stream with the sensitive membrane. An Ag/AgCl reference electrode (Ingold, type 373-90-WTE-ISE-S7) was also used. The potential was monitored by means of a Crison millivoltmeter (micro pH 2001) coupled to a Knauer recorder.

The pervaporation cell, designed in the laboratory (Fig. 1A), consisted of two chambers, a donor stream chamber (d) and an acceptor stream chamber (a) fitted with inlet and outlet orifices (h), and a thin membrane support (b). The volume of both the donor and acceptor chamber can be changed by placing the spacer (c) between the chamber and the membrane support. The whole module was made of methacrylate except for the membrane support, which was

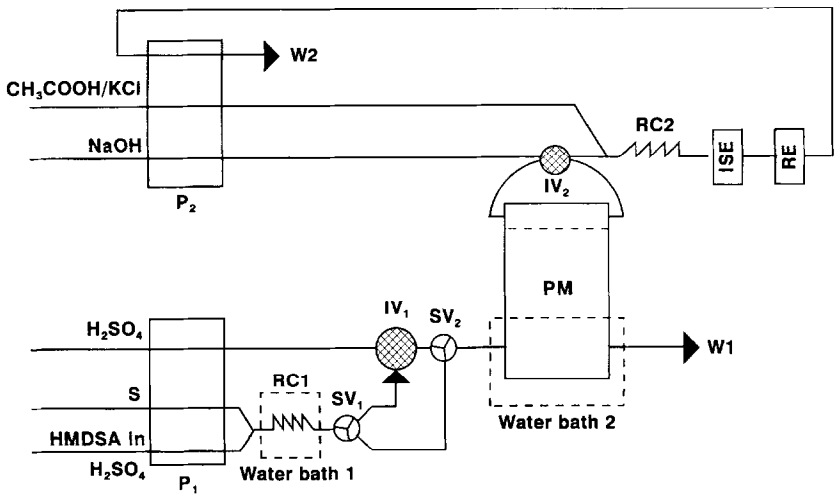

Fig. 2. Manifold with on-line pervaporation/potentiometric detection for the determination of fluoride after formation of a volatile derivative with HMDSA. Continuous propelling of the sample–HMDSA stream through the pervaporation module was used in the stopped-flow mode and the halting of the flow was accomplished by switching IV_2 to the filling position. The flow was restored when this valve changed to the injection position. S, sample; P, peristaltic pump; RC, reaction coil; IV, injection valve; SV, switching valve; PM, pervaporation module; ISE, fluoride-selective electrode; RE, reference electrode; W, waste.

made of PTFE. The upper and lower chambers and the membrane support were held together by means of four orifices (g), and a closer contact was achieved by screwing them with four screws (f) between two aluminium supports (e). The cross-sectional views of Fig. 1B show the dimensions and shape of the two chambers.

2.3. Manifold and procedure

Fig. 2 depicts the hydrodynamic system used. When working in the continuous mode, the sample or standard solution is mixed with HMDSA in acidic medium (H_2SO_4) to form the volatile derivative (trimethylfluorosilane, TMFS). The reaction takes place in a 300-cm coil thermostated at 90°C. This compound is injected into a H_2SO_4 stream and lead to the lower part of the pervaporation cell, which is thermostated at 80°C. There, the TMFS evaporates and diffuses through a PTFE membrane and is accepted by a NaOH stream. The outlet of the upper part of the separation module is merged with CH_3COOH–KCl stream through a 60-cm coil and led to the detector.

While operating in the stopped-flow mode the upper part of the module is used as the loop of the injection valve IV_2 and valves SV_1 and SV_2 are switched, thus the sample or standard solutions do not fill the injection valve IV_1 after formation of the volatile compound but merge directly with the sulphuric acid carrier and reach the lower part of the separation unit. The TMFS formed evaporates and diffuses through the membrane to be collected at a static NaOH stream at the upper part of the module while valve IV_2 is in the load position. After the required preconcentration time, the flow at the lower part is halted and IV_2 switched to the inject position. In this manner, the basic stream containing the fluoride is merged with the acetic acid–KCl solution and driven to the potentiometric cell for monitoring.

The PTFE membrane did not seem to deteriorate during a working day (ca. 12 h), but it was changed every day in order to avoid potential precision losses.

2.4. Sample treatment

Tap-water, well-water, fertilizers and ceramic industry waste water were used for validation of the method. The former two did not require treatment, but direct aspiration into the FI system. 0.5 g of each of the fertilizers were dissolved in 200 ml of doubly distilled water. The remaining solids were removed by filtration under vacuum in order to avoid clogging of the FI system. Solids were also removed from the samples from the ceramic industry by filtration under vacuum and the filtrate was directly introduced into the hydrodynamic system.

Table 1
Optimization of variables

Parameter	Range studied	Optimum value
CH_3COOH, M	0.15–0.3	0.2
KCl, M	1.0–3.0	1.0
HMDSA, %	1.0–2.0	1.5
H_2SO_4 (derivatizing medium), M	1.0–4.0	2.0
H_2SO_4 (carrier), M	0.5–2.0	1.0
NaOH, M	0.025–0.10	0.05
Temperature [a], °C	60–90	90
Temperature [b], °C	40–80	80
Loop, μl	100–1000	1000
Reaction coil length [c], cm	100–560	300
Donor flow-rate, ml/min	0.6–2.7	1.3
Acceptor flow-rate, ml/min	0.6–2.4	1.3
Flow-rate of the combined stream for the formation of TMFS, ml/min	0.5–1.8	0.5

[a] Temperature for the formation of the volatile compound; [b] Temperature for pervaporation of the volatile compound; [c] RC1 in the diagram of the manifold.

3. Results and discussion

A detailed study of the variables affecting the system was performed by using the univariate method. The range over which these variables were studied and the optimum values are listed in Table 1. The optimisation covered the following variables.

3.1. Chemical variables

Preliminary experiments were performed without the pervaporation cell but using the injection valve IV_2 for sample insertion (10 mg l^{-1} F^-) in order to optimize the response of the potentiometric sensor. Both a combined stream of CH_3COOH–KCl and two separate streams of CH_3COOH and KCl were checked. No difference was observed in the shape of the analytical signal so the combined channel was chosen for further experiments in order to minimise analyte dispersion. Decreased analytical signals were obtained by increasing the concentration of KCl up to 1.5 M, the signal remained constant above this value. The influence of the pH on the electrode response provided by the injected fluoride was assayed by changing the concentration of acetic acid while that of NaOH was kept constant. pH values between 4.5 and 5.0 gave rise to a constant and maximal signal. Above this value a loss of sensitivity was observed reaching at pH 6.0 a percentage of 18.4. A 0.2 M acetic acid solution providing a pH 5 was chosen for further work.

After the above-mentioned study the pervaporation cell was connected to the manifold in order to optimize both the formation of the volatile derivative and the performance of the separation module. The concentration of reagent used to form the volatile compound (HMDSA) and the acidic medium in which the reaction took place were optimized separately. No increase in sensitivity was observed for concentrations of H_2SO_4 and HMDSA higher than 2.0 M and 1.5%(v/v), respectively. The concentration of the alkaline acceptor has been claimed to influence the mass transfer process across the membrane, so it was studied by changing the concentration of NaOH in the acceptor stream also changing the concentration of the acetic acid solution in order to keep the pH of the solution reaching the selective electrode equal to 5.0. The best signal was provided by a 0.05 M NaOH solution. Above this value the signal decreased in such a way that a loss of 29% at 0.10 M NaOH relative to that obtained at 0.05 M NaOH was observed.

An increase in temperature had a positive effect on both the rate of volatile compound formation and that of the separation process as a consequence of a higher evaporation. As increased temperatures in the pervaporation module also had a negative effect on the membrane life, two separate water baths were used in order to fit the optimal performance of both processes. Thus, water bath 1 was kept at 90°C and water bath 2 at 80°C.

3.2. Variables of the pervaporation unit

After optimizing the working temperature, the other key variable of the separation module was the membrane. Three types of membrane were assayed. A cellulose membrane which was destroyed as soon as it came into contact with the NaOH; a PVDF which was more stable than the first type, and, finally, a PTFE membrane which provided the greatest stability to both the NaOH solution and temperature increases.

3.3. FIA variables

The injected volume had a marked influence on the analytical signal as it increased with increased volumes. 1000 μl was selected as a compromise between sensitivity and sampling frequency.

The length of the reaction coil for the formation of the volatile compound affected the degree of completion of the reaction. The reaction reached equilibrium in the 300-cm long RC1 (for a flow-rate of 0.5 ml min^{-1}), as longer reactors did not improve the signal. When the flow-rate of this combined channel was changed the signal was irreproducible for lower values and smaller for flow-rates above 0.5 ml min^{-1}.

The effect of the flow-rates of both the donor and the acceptor streams of the pervaporation cell was also studied.

The flow-rates of the donor and acceptor streams dramatically influenced the efficiency of the pervaporation process and thus the analytical signal obtained. A donor to acceptor ratio equal to 1 and low

Table 2
Features of the proposed method

Sample Introduction	Dynamic regime	Equation	r	Linear range (mg l^{-1})	R.S.D. (%)
Injection	Continuous	$Y = 158.33X - 225.92$	0.9998	40–100	2.60
Continuous	Stopped-flow	$Y = 65.71X - 1431$	0.9976	5–20	3.58

$X = \log[F^-]$ in mg l^{-1}; Y = mV.

flow-rates provided the best results but also low sampling frequency. The donor and acceptor flow-rates were set to 1.3 ml min^{-1} as a compromise.

The reproducibility of the sensor response increased by aspirating the waste from the reference electrode through pump P_2.

3.4. Stopped-flow mode

Preliminary experiments performed by halting the propulsion system that propelled the solutions in the upper part of the separation module (as a way of increasing efficiency of the mass transfer process) gave rise to two phenomena: (a) irreproducibility of the sensor response by changing the dynamic to the static regime and vice versa. (b) The static NaOH solution in the separation unit moved backwards, so air bubbles appeared in the system and no signal could be obtained. This effect was caused by expansion of the pump tubes when the propelling system was halted. Both shortcomings were circumvented by locating the injection valve IV_2 as shown in Fig. 1. In the filling position of the valve the flow through the system is continuous, except in the loop of the valve, which constituted the upper chamber of the pervaporation cell; the flow through it is restored by switching the valve to the inject position. A continuous passage of the sample–HMDSA mixture through the lower chamber of the pervaporation module was also established in order to ensure maximal concentration of the volatile product in the cell (for a given concentration of the analyte in the sample) and thus also both maximal evaporation and mass transfer across the membrane.

Stopped-flow times of the NaOH solution in the upper part of the pervaporation module between 0 and 5 min were assayed. Increased signals were obtained as the stop interval increased and a stop-time of 5 min was chosen as a sensitivity/sample throughput compromise.

An additional drawback appeared when real samples were used. The higher density and viscosity of these samples caused a small overpressure in the dynamic system which resulted in increased level in the lower part of the pervaporation cell, and so the sulphuric mixture reached the membrane, which was destroyed instantly. In order to overcome this problem, the waste W_1 was aspirated through P_1 at a flow-rate equal to that of the inlet stream.

Table 3
% Decrease in the analytical signal produced by interferents

Ion added	Analyte-to-foreign species ratio [a]			
	1:1	1:5	1:10	1:100
Al(III)	0.7	52.7	66.4	91.1
Fe(III)	–	0.8	7.6	39.4

[a] Concentration of fluoride, 60 mg l^{-1}.

3.5. Features of the method

Two calibration graphs were obtained by using both injection of the sample-HMDSA mixture for the continuous-flow mode and continuous aspiration of the sample-HMDSA mixture for the stopped-flow mode. The results obtained in terms of equation, linear range, correlation coefficient and precision, studied as repeatability and expressed as relative standard deviation, are listed in Table 2.

The sampling frequency was 8 h^{-1} and 6 h^{-1} for the injection and the continuous introduction/stopped-flow mode, respectively.

Table 4
Results obtained by application of the method

Sample	Fluoride found (mg l^{-1})	Mean recovery (%), (R.S.D., %)	
		Addition of 10 mg l^{-1} [a]	Addition of 50 mg l^{-1} [b]
Tap water	–	90.00 (2.66)	93.62 (1.46)
Well water	–	92.00 (2.54)	89.36 (3.45)
Fertilizer 1	–	96.00 (4.17)	87.23 (2.44)
Fertilizer 2	6.0	91.59 (2.04)	100.36 (3.39)
Fertilizer 3	8.5	103.54 (0.85)	100.64 (1.04)
Ceramic industry wastewater 1	5.9	101.03 (4.03)	96.78 (2.38)
Ceramic industry wastewater 2	8.2	100.74 (0.89)	89.64 (1.86)
Ceramic industry wastewater 3	9.0	106.09 (3.07)	90.04 (0.72)

[a] Using the stopped-flow mode.
[b] Using the continuous mode.

3.6. Study of interferences

The interference caused by the presence of Al(III) and Fe(III) was studied by monitoring the decrease in the analytical signal from a standard solution of the target analyte of 60 mg l^{-1}, which contained different concentrations of the above mentioned cations. Table 3 shows the results of this study. No interference was observed when the concentration of aluminium present was the same as that of fluoride; while iron(III) did not interfere when present at a concentration 5 times that of fluoride.

3.7. Application of the method to real samples

To show the applicability of the method to real samples, it was applied to the determination of fluoride in tap water, well water, fertilizers and ceramic industry wastewater by using the injection/continuous-flow mode and the continuous sample aspiration/stopped-flow mode. Table 4 shows the concentrations found, mean recovery and R.S.D. ($n = 3$) for each sample. The recovery ranged between 87.23 and 106.09% with R.S.D. values between 0.72 and 4.17%.

Final remarks

The pervaporation/determination method for fluoride developed by using the pervaporation module designed and built in our laboratory provides a quite interferentfree method for this analyte. The sensitivity of the method can be manipulated by changing the stopped-flow interval. Pervaporation has thus proved to be an effective process for removal of the volatile analytes (or reaction products) from complex matrices.

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