

Simultaneous determination of potassium and total fluoride in toothpastes using a SIA system with two potentiometric detectors

R. Pérez-Olmos*, J.C. Soto, N. Zárata, I. Díez

Lab. de Química Analítica, EUITI, Universidad del País Vasco, Plaza de la Casilla 3, 48012 Bilbao, Spain

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Abstract

A sequential injection analysis (SIA) system has been developed for the first time to quantify potassium and total fluoride in toothpastes and gels used to prevent both dentinal hypersensitivity and dental caries. To enable this simultaneous determination, potentiometric detection, using a conventional fluoride electrode and a tubular potassium selective electrode, formed by a PVC membrane containing valinomycin as ionophore, was carried out. A manifold that uses a three-way solenoid valve was designed. The former under binary sampling conditions, provides reproducible mixing ratios of two solutions. This fact facilitates that the system automatically generates, on-line, the calibration curves required by the analytical procedure. The calibration ranged from 1.0×10^{-4} to 1.0×10^{-3} mol L⁻¹ for both potassium and total fluoride determinations. The R.S.D. (11 readings) resulted to be less than 1.5% for both determinations. Off-line studies related to the dissolution of the solid samples, the transformation of monofluorophosphate in fluoride, the elimination of organic matrix interference onto the plastic membrane of the potassium electrode, and the selection of the most adequate TISAB solution for fluoride determination, were also considered. A sampling rate of 18 samples h⁻¹ for both determinations was attained, their precisions and accuracies being statistically indistinguishable from those achieved by atomic emission spectroscopy (for potassium determination) and by a conventional batch potentiometry (for total fluoride determination) adopted as reference techniques.

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1. Introduction

It is well known that the fluoride ion has a critical role in preventing tooth decay. Toothbrushing with fluoride ion-containing toothpaste is by far the most common way of caries control. Nowadays, the main sources of fluoride in toothpaste are sodium fluoride and monofluorophosphate (MFP). Different methods of analysis for the determination of fluoride plus MFP (after transformation in fluoride by hydrolysis in presence of hydrochloric acid) in toothpaste have been developed. Some of these methods were potentiometric procedures in batch analysis [1–17]. On the other hand, the fluoride selective electrode was used as potentiometric detector in flow injection analysis (FIA) [18–20] and SIA [21] flow techniques. To a lesser extent, gas chromatography [22,23] and atomic absorption spectrometry [24] were used. Some works, comparing these methods, have been

published [25–27]. To determine simultaneously fluoride and MFP in toothpaste, ion-chromatography [28–32] and capillary electrophoresis [25,33–35] have been proposed. Since FIA is a very effective technique for the automation of chemical analysis and it makes possible multiparametric detection, two FIA manifolds were developed for the simultaneous determination of fluoride and MFP using spectrophotometric detection [36], and fluoride, MFP and orthophosphate using both spectrophotometric and potentiometric detection [37].

Dentinal hypersensitivity is a common unpleasant sensation and many people complain about having teeth that are sensitive to hot or cold liquids or to tactile stimuli. Most cases can be easily treated at home, by brushing with a toothpaste containing a potential desensitizing agent. At present, potassium nitrate is the most utilized desensitizer contained in the toothpastes marketed in many countries. In spite of this, other potassium salts such as chloride [38], oxalate [39,40] or citrate [38] have been recently used in clinical trials. A method based on the use of a nitrate selective electrode for the determination of potassium nitrate in products, used for the treatment of dentinal hypersensitivity, has

* Corresponding author. Tel.: +34 946 014 428; fax: +34 946 014 300.

E-mail address: gappeolr@lg.ehu.es (R. Pérez-Olmos).

been published by some of us [41]. Simultaneous determination of nitrate and MFP in toothpaste, by ion-chromatography, has been developed [42,43].

Nowadays, it is possible to find in the market toothpastes containing compounds used to prevent both caries and dental hypersensitivity. For that reason, in this work and for the first time, an economic, rapid and simple method for the on-line simultaneous determination of total fluoride and potassium contained in toothpastes based on a SIA manifold is proposed. It uses a commercial fluoride selective electrode and a tubular potassium selective electrode, constructed in the laboratory, as potentiometric detectors.

2. Experimental

2.1. Reagents and solutions

For the preparation of the membrane of the potassium tubular potentiometric detector, valinomycin ref. 94675, bis(2-ethylhexyl) sebacate ref. 84818, potassium tetrakis(4-chlorophenyl)borate ref. 60591, all of them from Fluka (Steinheim, Switzerland), and tetrahydrofuran ref. 1.09731 from Merck (Darmstadt, Germany) were used. For the conductive support, a mixture (1:1.2 w/w) of graphite powder ref. 4206 from Merck and a non-conductive epoxy resin (1 g of Araldite M with 0.4 g of hardener REN HY 5162) from Vantico España S.L. (Barcelona, Spain) were utilized.

In the flow system proposed, a TISAB solution was used as ionic strength adjuster/carrier solution, and also as inner electrolyte solution in the reference electrode for both determinations. The ionic strength adjuster for the fluoride and the potassium determinations was a TISAB solution of pH 8.2. This solution was prepared by dilution of 8.4 mL of hydrochloric acid, ref 1.00317, in 500 mL of deionized water and by dissolving 24.2 g of tris(hydroxymethyl)aminomethane, ref. 1.08382, and 23.0 g of sodium tartrate 2-hydrate, ref. 1.06663, all of them from Merck. This mixture was under stirring and heating, and transferred to a volumetric flask of 1000 mL. The volume was adjusted to 1000 mL with deionized water. The ionic strength adjuster solution contained a 1.0×10^{-8} mol L⁻¹ potassium fluoride (Merck ref. 1.04994). The stock solution

used to prepare, on-line, the calibration curves of both ions was a 1.0×10^{-3} mol L⁻¹ potassium fluoride solution prepared by rigorous weighing out of the solid in deionized water.

A 0.1 mol L⁻¹ potassium chloride stock solution (Merck ref 1.04933) was prepared for the potassium determination by using atomic emission spectroscopy. Less concentrated solutions, for the preparation of the calibration curves, were obtained after dilution of the previous one. A 1.0 mol L⁻¹ hydrochloric acid solution was also prepared. For the fluoride batch determination a 0.1 mol L⁻¹ sodium fluoride stock solution (Merck ref. 1.06449) was prepared and a TISAB solution, ten times more concentrated than the solution utilized in the SIA system, was used.

All solutions were prepared with deionized water (conductivity <0.1 μ S cm⁻¹) and analytical grade chemicals were used without any additional purification.

2.2. Apparatus and electrodes

Two Orion 720 potentiometers, sensitivity ± 0.1 mV, from Orion Research (Cambridge, USA), were used for measuring the difference of potential. The reference electrode was a double junction AgCl/Ag (Orion 90-02-00) containing in the outer compartment a solution formed by 1 mL of the TISAB/carrier solution and 10 mL of a 1 mol L⁻¹ sodium chloride solution diluted in 100 mL of deionized water. The potassium selective electrode was a tubular potentiometric detector with PVC membrane and without internal reference solution. The membrane preparation was carried out following a previously described [44] methodology, by mixing 1% (w/w) of valinomycin, as ionophore, 65.8% (w/w) bis(2-ethylhexyl)sebacate, as plasticizer, 0.2% (w/w) potassium-tetrakis(4-chlorophenyl)borate, as membrane additive, and 33.0% (w/w) of PVC previously dissolved in tetrahydrofuran. The membrane solution was directly applied and deposited in the conductor surface, made up of a mixture of epoxy resin with graphite powder, of the central electrode hole. The fluoride selective electrode was an Orion 9409. Both selective electrodes were connected to home-made tubular stainless steel ground electrodes in order to eliminate static electricity pulses. The fluoride selective and the reference elec-

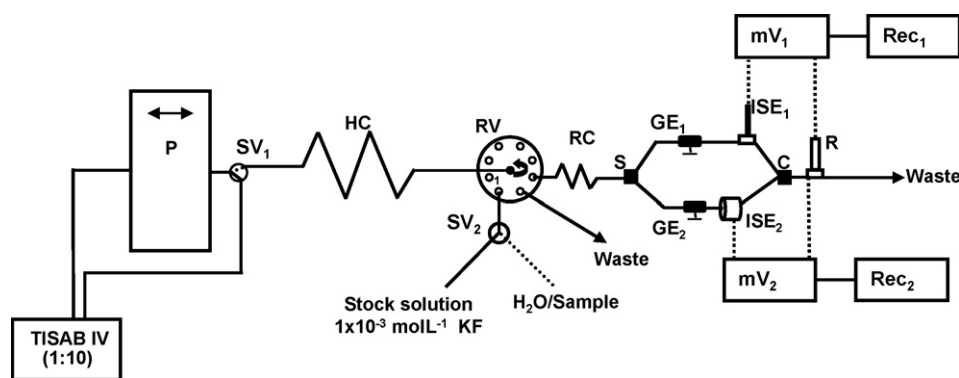


Fig. 1. Schematic representation of the potentiometric SIA system developed. P: peristaltic pump; RV: multiposition rotatory valve; SV₁, SV₂: three-way solenoid valves; HC: holding coil; RC: reaction coil; S: splitting; C: confluence; GE₁, GE₂: ground electrodes; ISE₁: fluoride selective electrode; ISE₂: potassium tubular electrode; R: reference electrode; mV₁ and mV₂: decimilivoltmeters; Rec₁ and Rec₂: recorders.

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