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Ultra-sensitive Flow Injection Analysis (FIA) determination of calcium in ice cores at ppt level

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Abstract

A Flow Injection Analysis (FIA) spectrofluorimetric method for calcium determination in ice cores was optimised in order to achieve better analytical performances which would make it suitable for reliable calcium measurements at ppt level.

The method here optimised is based on the formation of a fluorescent compound between Ca and Quin-2 in buffered environment. A careful evaluation of operative parameters (reagent concentration, buffer composition and concentration, pH), influence of interfering species possibly present in real samples and potential favourable effect of surfactant addition was carried out. The obtained detection limit is around 15 ppt, which is one order of magnitude lower than the most sensitive Flow Analysis method for Ca determination currently available in literature and reproducibility is better than 4% for Ca concentrations of 0.2 ppb.

The method was validated through measurements performed in parallel with Ion Chromatography on 200 samples from an alpine ice core (Lys Glacier) revealing an excellent fit between the two chemical series. Calcium stratigraphy in Lys ice core was discussed in terms of seasonal pattern and occurrence of Saharan dust events.

Keywords: Flow injection analysis; Calcium; Ice cores; Alps; Antarctica

1. Introduction

An increasing interest was recently devoted to the chemical analysis of ice cores as paleo-environmental and paleo-climatic archives in understanding climate global change. Indeed, these information are stored in ice core stratigraphies at very high temporal resolution, even sub-annual, for long time periods, up to 900 kyr (see for instance [1–4]). In particular, the analysis of trace chemical species provides a unique tool to achieve information on paleo-atmospheres revealing changes in load and chemical composition of atmospheric aerosol as a response to climatic forcing [5,6]. Ice core ionic composition is usually measured by ion chromatography (IC) methods on discrete samples; this procedure is time consuming and the temporal resolution is limited by the sub-sampling and by the maximum number of samples that can be analyzed in a reasonable time period. In order to overcome this difficulty, several continuous methods, named Continuous Flow Analysis (CFA) were recently developed. They are usually built by coupling Flow Injection Analysis (FIA) techniques with spectrophotometric or spectrofluorimetric detectors. CFA analysis can be in field carried out minimizing sample handling and contamination risk by storage and transport. Several chemical markers have been analysed by CFA methods along GRIP (Greenland Ice Core) [7,8], EPICA Dome C (European project for Ice Coring in Antarctica—Dome C) [1,5] and EPICA DML (Dronning Maud Land) ice cores [6].

CFA measurements of calcium content were the earliest to be developed because this parameter is generally considered as a reliable, though not unequivocal, crustal marker in ice cores. In Greenland and alpine ice cores, calcium shows well defined summer concentration maxima and winter minima due to different aerosol transport mechanisms in the two seasons and, for Greenland, to the greater extent of source areas in summer (e.g. [9,10]). Due to the high snow accumulation generally characterising Greenland and alpine sites, Ca seasonal cycle can be used for a stratigraphic dating of the snow layers [11,12].

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A CFA method for Ca determination was also used for Antarctic ice cores. In this case, due to the longer distance of Ca source areas, its measurement is reliable only in samples corresponding to glacial periods, when the high dust content leads to high Ca concentrations in the atmosphere and, consequently, in the snow layers [13]. In samples corresponding to interglacial periods, the measured Ca concentrations are definitely lower, generally on sub-ppb level, which is lower than the detection limit of currently available methods [14]. Therefore, small Ca variations in warm periods cannot be evaluated with sufficient accuracy and reproducibility.

The purpose of this paper is an optimisation of the method based on the formation of a fluorescent compound between Ca and the reagent Quin-2, in order to achieve better performances, in particular a lower detection limit which revealed to be around 15 ppt (2σ), one order of magnitude lower than the most sensitive CFA method for Ca determination reported in literature to date [14]. A method validation was also performed through measurements carried out in parallel with Ion Chromatography on an alpine ice core (Lys Glacier, Monte Rosa massif). Ca stratigraphy in Lys ice core was studied in order to point out Ca seasonal pattern and the occurrence of Saharan dust events.

2. Experimental

2.1. Method optimisation

The FIA method for calcium determination here developed is based on the formation of a fluorescent complex of Ca with 8-amino-2-[(2-amino-5-methylphenoxy)methyl]-6-methoxyquinoline-*N*,*N*,*N*′,*N*′- tetraacetic acid (Quin-2) [14,15].

The complexing agent, buffered at about pH 6.5, is added to the sample and, after a suitable reaction time, Ca content is measured by the fluorescence of the produced complex at $\lambda_{em} = 489$ nm by a spectrofluorimeter.

All the reagents were purchased at the highest available purity grade and all solutions were prepared with UHQ water (resistivity > 18 MΩ) obtained with a Millipore-MilliQ system and continuously recycled by a UHQ Simplicity 185 device.

Fig. 1 shows a schematic depiction of the method setup. The sample is injected by a PTFE 6-port valve (Rheodyne type 50) in an ultrapure water carrier at the flow of 0.85 mL min^{-1}. After the injection valve, the reagent (0.13 mL min^{-1} Quin-2 2.4×10^{-5} M in piperazine-*N*,*N*′-bis (2-ethan-sulphonic) acid (PIPES) buffer 1.25×10^{-2} M,) is mixed with the carrier. The mixing coil (85 cm, i.d. 0.5 mm) is shielded from light to prevent photolytic decomposition of the produced fluorescent complex. A computerised Shimadzu fluorimeter (SPD-10AV), equipped with a Xe lamp (150 W) and a 12 μL volume square quartz cell, was used as detector. Fluorescence was measured at 489 nm ($\lambda_{exc} = 334$ nm) where the analyte/blank signal revealed to be highest (see Emission and excitation spectra in the electronic supporting material). Quin-2 and PIPES at reagent grade were purchased from Fluka; pH was adjusted with a suprapur Merck sodium hydroxyde solution. Both reagent and Ca standard solutions for calibration were daily prepared; Ca standards at ppt–ppb level were prepared by diluting a 1000 ppm Merck standard solution.

Fig. 2a shows sensitivity changes as a function of Quin-2 concentration. Since both method sensitivity and background noise (evaluated from blank reproducibility) increase as Quin-2 concentration increases, a concentration of 2.4×10^{-5} M was chosen as the best compromise between sensitivity and reproducibility.

The highest fluorescence signal was found to occur at pH 6–7 [15]. Several solutions were tested as buffers in this range (precisely, at pH 6.5): piperazine-*N*-*N*′-bis(2-ethan-sulphonic) acid (PIPES), Tris–HCl, Imidazole, phosphate and citrate buffer. The influence of buffer typology on measurement sensitivity can be observed in Fig. 2b where sensitivity values were reported as percentages of the signal obtained with the PIPES buffer taken as 100%. In order to achieve an accurate evaluation of the sensitivity, each point reported in the figure represents the slope of a five-point calibration line calculated for each concentration buffer. The same procedure was applied to evaluate sensitivity as function of the chosen buffer concentration (Fig. 2c) and reagent pH (Fig. 2d). PIPES buffer was chosen since it shows the highest sensitivity even if only of a few percentage units with respect to the other buffers, except for citrate. Citrate buffer showed a definitely lower sensitivity, probably because of the formation of a competitive Ca complex with citrate. PIPES buffer had already been used in Ca fluorescence measure-

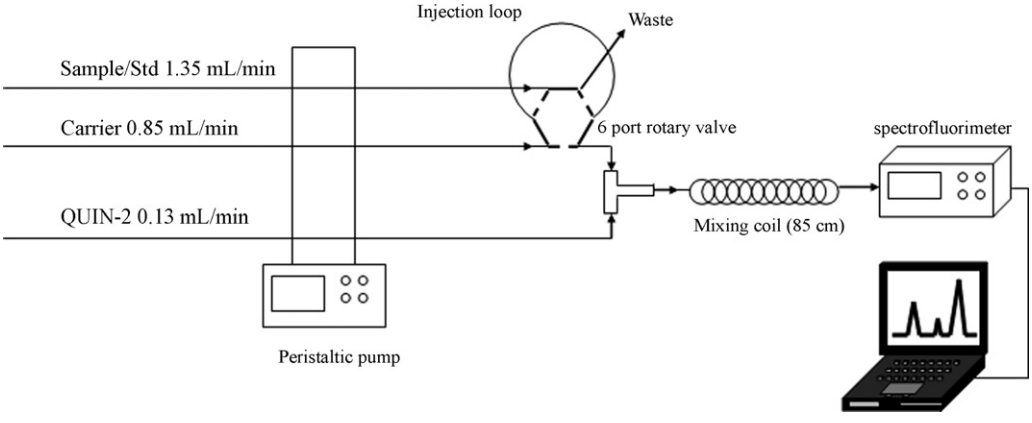

Fig. 1. Flow chart of the FIA-spectrofluorimetric method for calcium determination.