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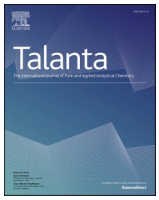

An upgraded CFA – FLC – MS/MS system for the semi-continuous detection of levoglucosan in ice cores

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ABSTRACT

A new Continuous Flow Analysis (CFA) system coupled with Fast Liquid Chromatography – tandem Mass Spectrometry (FLC-MS/MS) has been recently developed for determining organic markers in ice cores. In this work we present an upgrade of this innovative technique, optimized for the detection of levoglucosan in ice cores, a crucial tracer for reconstructing past fires. The upgrade involved a specific optimization of the chromatographic and mass spectrometric parameters, allowing for a higher sampling resolution (down to 1 cm) and the simultaneous collection of discrete samples, for off-line analysis of water stable isotopes and additional chemical markers. The robustness and repeatability of the method has been tested by the analysis of multiple sticks of ice cut from the same shallow alpine ice core, and running the system for several hours on different days. The results show similar and comparable trends between the ice sticks. With this upgraded system, a higher sensitivity and a lower limit of detection (LOD) was achieved compared to discrete analysis of alpine samples for levoglucosan measurements. The new LOD was as low as 66 ng L^{-1}, a net improvement over the previous LOD of 600 ng L^{-1}.

1. Introduction

Ice cores are considered one of the most useful climate archives as they contain many different chemical proxies in a simple chemical matrix making it possible to measure them simultaneously. Information on past synoptic circulation, atmospheric composition, and even past fire activity can be found within ice cores, furnishing an unprecedented perspective of the Earth's climate history, where both forcing and climate signals have been preserved [1,2]. However, one of the main challenges the paleoclimate scientific community is facing is the development of new analytical systems and improvements to existing ones, to obtain higher-resolution measurements of chemical markers in ice cores. Typically, ice core analyses are conducted after manual decontamination, melting and analysis of discrete samples. This can be very time-consuming and reduces temporal resolution to the size of the discrete sample. To overcome this drawback, Continuous Flow Analysis (CFA) systems were introduced in the early '90s [3].

CFA systems continuously melt a longitudinal sub-section of an ice core, and carry out on-line measurements of several chemical and physical parameters to obtain a high-resolution signal. Given its great advantages, mainly represented by the high resolution (down to 1 cm), reduced time effort in ice core processing, limited risk of contamination, and large amount of data which can be extracted from ice cores, the CFA is widely employed in several laboratories [4–11]. Optimization of the set-ups is managed according to the specific needs, allowing for a large amount of data which can be extracted from ice cores in a single analytical run.

In this work, an innovative and upgraded coupling between CFA and Fast Liquid Chromatography tandem Mass Spectrometry (FLC – MS/MS) is presented. Although the first efforts to couple a continuous melting device with analytical techniques date back to the early 1990s [3], it is only in the last 20 years that the coupling of Continuous Flow Analysis (CFA) with chromatographic techniques [12–17] was successfully applied. The advantages of CFA, combined with the accuracy, precision,

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and low detection limits of chromatographic methods, have permitted researchers to achieve higher sensitivities and higher sample throughputs [16]. Moreover, since the first coupling of Fast Ion Chromatography (FIC) with a CFA system [14], the analytical time resolution has increased (from one measurement every minute to one measurement every 30 s), and the chromatographic performance has seen effective improvements. Nevertheless, despite these improvements, the coupling of Ultra High Performance Liquid Chromatography (UHPLC) - mass spectrometry with CFA is a valuable novelty for ice core analysis, particularly for the semi-continuous detection of biomass burning tracers [11].

Our CFA system allows us to perform continuous measurements of insoluble dust particles (concentration and size distribution), meltwater electrical conductivity, and dissolved organic compounds (in semi-continuous manner). In this work, the previous method developed to analyze specific Biomass Burning (BB) tracers such as Vanillic acid (VA) and Syringic acid (SyA) with a spatial resolution in the ice of 1.5 cm [11], has been optimized for the quantification of levoglucosan, achieving a spatial resolution down to 1 cm. However, this technology can potentially be employed to detect any organic compound, following revision of the chromatographic and mass spectrometric parameters.

Here we present improvements to the system [11] since 2021, that carried out semi-continuous measurement of phenolic compounds (VA and SyA) in alpine ice cores, with optimization for levoglucosan determination. This method could represent a significant step forward to address the wide lack of data for organic tracers in ice cores.

Levoglucosan has long been considered a key tracer of BB, because it is only emitted from the combustion of cellulose and hemicelluloses [18–23], although its applicability in chemical mass balance has been recently questioned [24]. It appears to be chemically reactive in the atmosphere and cannot distinguish the type of vegetation burnt, as VA and SyA can do [11,24]. However, once it is emitted into the atmosphere, it can undergo long range transport to ice caps where it can be preserved in snow and ice, providing a fingerprint of fire activity on a regional to global scale [25]. High-altitude alpine glaciers, due to their proximity to urban areas compared to polar regions, can preserve higher concentrations of levoglucosan in the ice. To-date, only a few works have focused on levoglucosan in glacier snow and ice, and their sampling sites are sparely distributed worldwide. For the European Alps, results have been reported for Col du Dome ice core only [26], and the method applied by Legrand et al. in this case was the one initially deployed for aerosol analysis, which employed the liquid chromatography and a NaOH-gradient eluent. Levoglucosan concentrations of the melted ice samples were found below the detection limit (30 μg L^{-1}), thus samples were preconcentrated by a factor of 50 through evaporation, achieving a detection limit of 0.6 μg L^{-1} for a 100 mL of sample [26].

2. Materials and methods

2.1. Ice core site characteristics

The Grand Combin (GC) ice core was drilled from the summit plateau of the Corbassière glacier (45.98 N, 7.28 E), in the saddle between Grand Combin de Grafeneire and Grand Combin de Valsorey (Switzerland, 4100 m a.s.l.), reaching a depth of 25.95 m. The ice core sample analysed with the new CFA – FLC/MS/MS coupled system did not include the first 11 m of firn, due to the inappropriate density to be managed by the continuous melting system.

The entire ice core was characterized by the presence of higher density refrozen ice lenses, due to melting – refreezing processes which likely took place in summer 2019 [27].

2.2. Ice core processing for CFA

Before analysis, ice cores are thoroughly cleaned and cut, following different schemes according to specific needs and to the amount of material available (i.e., melt head dimensions, type of analysis to be conducted, further comparative measurements). Within this work, the deepest part of a shallow ice core drilled at the Corbassière glacier (GC) (0.075 m diameter and 25.70 m length), from 24.35 m to 25.10 m, was processed to obtain two parallel sections (0.032 × 0.032 × 0.70 m), to allow an evaluation of the method reproducibility (Fig. 1A). The shallowest part of the same section, from 11.56 m to 21.85 m, was cut according to the scheme in Fig. 1B, saving some ice for the archive and another section for biological analysis (a description of the cutting scheme is reported in Table 1). The ice was cut with a modified commercial band saw, modified with a decontaminated stainless-steel blade over a polyethylene tabletop, with guide rails for cutting. The table, the rails, and the blade were carefully cleaned with acetone and methanol to remove contamination before every use. All the exposed ice surfaces were rapidly scraped with a stainless-steel knife cleaned with 0.1% ultra-pure HNO_3 (Romil, Cambridge, UK), and carefully dried after each use. The knife was used to remove the thin, outer contaminated ice layer, and contamination from the two base surfaces which were to be placed directly on the melting head. Several mm of ice from each end were removed to ensure perfect contact with the melting head surface. The ice sections (*bags*) were stored in clean PTFE bags until analyses. Each sample was then inserted into a polyethylene holder and placed on the melting head. Each run was preceded by two 0.05 m long sections of frozen Ultra-Pure Water (UPW, Purelab Ultra-Analytic, Elga LabWater, High Wycombe, UK) to clean the whole system, monitor the blank level, and provide a baseline before the sample melting. For the same reasons, the last bag of the day was followed by two 0.05 m pieces of UPW. No UPW sticks were put between the bags within the same run, to avoid dilution of the signal between samples.

2.3. CFA system

The CFA developed and employed at the laboratory of Ca' Foscari University and Institute of Polar Sciences (CNR) of Venice is designed for the continuous detection of insoluble dust particles, organic compounds and off-line quantification of heavy metals, major ions and water stable isotopes (Fig. 2). The melthead in use features a square cross-section with an inner and outer collection area separated by a 0.002 m high triangular ridge, as the one adopted in Copenhagen [7]. Four external lines (purple lines in Fig. 2) exiting from the 8e-6 m^2 outer area are connected to a fraction collector that samples at a flow rate of 1 mL min^{-1} the outermost meltwater stream for off-line quantification of water stable isotopes, as these are not affected by any possible external contamination of the core. The remaining 13 mL min^{-1}, are directed instead to the waste. The innermost melt flow passing through a 0.0015 m central hole within the melthead inner collection area, is directed to a first peristaltic pump (grey line in bold, Fig. 2), and is split after the first conductimeter (c_1). From this point onward, part of the stream is directed to the fraction collector at a flow rate of 4.9 mL min^{-1} (blue line in bold, Fig. 2), and the rest (black line in bold, Fig. 2) is degassed by a first flat cell triangular debubbler (~200 μL volume), and pushed by a second peristaltic pump through a five-port manifold, where two main lines (red and green lines in Fig. 2) split further the flow. Thus, the stream is in part directed to the FLC – MS/MS system (red line), with a flow rate of 0.268 mL min^{-1}, and only ca. 75% of the core is analysed in these analytical conditions. At the moment, this flow is optimal to obtain the complete load of sample loops but future implementation can be performed to minimize the dead volume, so reducing sample leaking. The rest of flow passed through the laser particle counter and ended up with the fraction collector (green line) with a flow rate of 1.39 mL min-1 (Fig. 2). A second debubbler is placed along the red line as precaution to guarantee a constant, minimal, and mostly air bubbles-free flow rate to the chromatographic system, since air can damage the stationary phase of chromatographic columns by altering the backpressure of FLC system. The use of a fraction collector makes the CFA a hybrid system, allowing

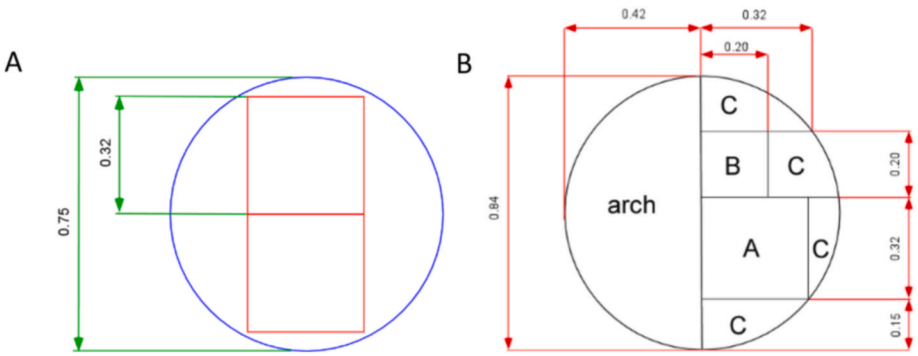

Fig. 1. a,b Cutting schemes for the Grand Combin ice core (a: deep part, from 24.35 m to 25.10 m; b: shallow part, from 11.56 m to 21.85 m).

Table 1
Description of the cutting scheme (Fig. 1B).

SECTION DESCRIPTION	dimensions	surface (m^2)	Mass (kg m^{-3})	
			d = 500 kg m^{-3}	d = 900 kg m^{-3}
TOT SURFACE	ray 0.042 m	5,50E-03	2,76E+04	4,99E+04
Melter stick (A)	0.032x0.032 m^2	1,02E-03	5,10E+03	9,20E+03
Discrete samples stick (B)	0.02x0.02 m^2	4,00E-04	2,00E+03	3,60E+03
biochemistry (∑c)	residuals	1,35E-03	6,80E+03	1,21E+04
ARCHIVE	1/2 section	2,75E-03	1,38E+04	2,49E+04

us to collect discrete samples for off-line analysis. A switching valve allows to switch from sample to UPW stream, and is normally employed at the end of the daily runs (to clean the system) or if the ice sticks get stuck during the melting due to cutting defects, in order to avoid the overcome of the debubblers and the entrance of air in the system.

The employing of debubblers within a CFA system is essential to remove the about 10% air naturally found in ice. The design of this central component of the CFA detection system may be an "open" pipette type with a holed lid, which is applied to shield against contamination from the laboratory, or a sealed flat triangular cell, as the one done by Bigler et al. (2011) [7].

A home-made modular software has been developed in LabView 2015, for easier management of the melting and distribution line components. This home-made software controls the draw wire sensor, which is a sensor attached to a stainless-steel rope for the high precision measurements of the melting speed and ice height, the peristaltic pumps, the fraction collector for discrete sampling, the conductimeters, and the laser particle counter (Abakus® Klotz). A proportional-integrative-derivative (PID) controller has been adopted to control heating of the melting head when inside the vertical freezer.

Starting from the set-up realized in 2021 for the determination of vanillic and syringic acids in ice cores [11], we addressed the need to enhance the spatial resolution of the analysis without affecting the dispersion of the analytical signals, while optimizing the chromatographic and mass spectrometric conditions for levoglucosan analysis. Therefore, we reduced the melting speed from 3 to 2 cm min^{-1}, without modifying the flow rate which feeds the FLC system, by splitting the innermost melt water flow before entering the first debubbler, and directing the exceeding flow (4.9 mL min^{-1}) to the autosampler for the collection of discrete aliquots destinated to off-line analysis of additional chemical markers. The remanent 1.66 mL min^{-1}, net of the debubbler overflow (0.57 mL min^{-1}), is further divided in two: 1.39 mL min^{-1} passing through the laser particle counter and being collected by the autosampler, and 0.268 mL min^{-1} destinated to the FLC system's feeding, where two loops (100 μL each) are loaded alternately every 30 s, making elution occurring in one out of the two employed columns at time, while the other is cleaning and equilibrating. Further details on the FLC-MS/MS coupling are reported in a previous study [11].

In this way, the innermost melt water flow losses are contained to the 0.57 mL min^{-1} of overflow from the debubbler, and to the 0.07 mL min^{-1} excess for loops loading, representing a total loss of 8.9% (Table 2). This is a necessary buffer in the presence of repeated density changes (e.g., due to the presence of ice lenses along the ice sticks), to avoid the air to reach the system due to frequent melt rate fluctuations.

2.4. Fast liquid chromatography coupled with triple quadrupole mass spectrometry

The chromatographic system used in this work is the Thermo Scientific Dionex UltiMate 3000 Rapid Separation LC system, consisting of two separate dual-gradient Rapid Separation Pumps (DGP-3600RS, Thermo Fisher Scientific). A column oven (DGP-3600RS, Thermo Fisher Scientific) maintains the two C18 Columns at 70 °C. Two 6-Port Valves are used to load and inject the samples every 30 s, and an additional divert valve is located before the mass spectrometer. An API 4000 triple quadrupole mass spectrometer (Applied Biosystems/MDS SCIEX, Toronto, Ontario, Canada) equipped with a Turbo V source has been employed to determine levoglucosan. The quantification was performed using $^{13}C_6$ levoglucosan as internal standard. Data was collected in negative ion mode by multiple reaction monitoring (MRM) with a 50 ms dwell time/transition. In the MRM acquisition mode, the first quadrupole (Q1) selects the parent ion while the third quadrupole (Q3) selects the fragment (daughter) ion of interest; both Q1 and Q3 were set at unit resolution (a peak width of 0.7 ± 0.1 amu at 50% of maximum peak height). The transition monitored and the parameters, such as collision energy and collision cell exit potential for levoglucosan and labelled levoglucosan, are reported by Gambaro et al. [1]. To improve the number of acquisition points, the number of transitions was reduced to three MRM transitions for levoglucosan (161 > 113, 161 > 101, 161 > 71) and two for the internal standard (167 > 118, 167 > 105). The most intense transitions (161 > 101 and 167 > 105) were used for quantification of levoglucosan.

3. Results and discussion

3.1. Chromatographic and spectrometry optimization

The method development for organic compounds using FLC-MS/MS is primarily about optimizing the mass spectrometric and chromatographic parameters: stationary phase (column), mobile phases (eluents), flow rate, linear gradient program, and eventually a post column make up flow to improve signal intensity.

The optimization of the chromatographic separation was performed by testing several commercially available HPLC columns and by varying the mobile phase. Three commercially available HPLC C18 columns were tested considering selectivity and signal tailing: Synergy Hydro

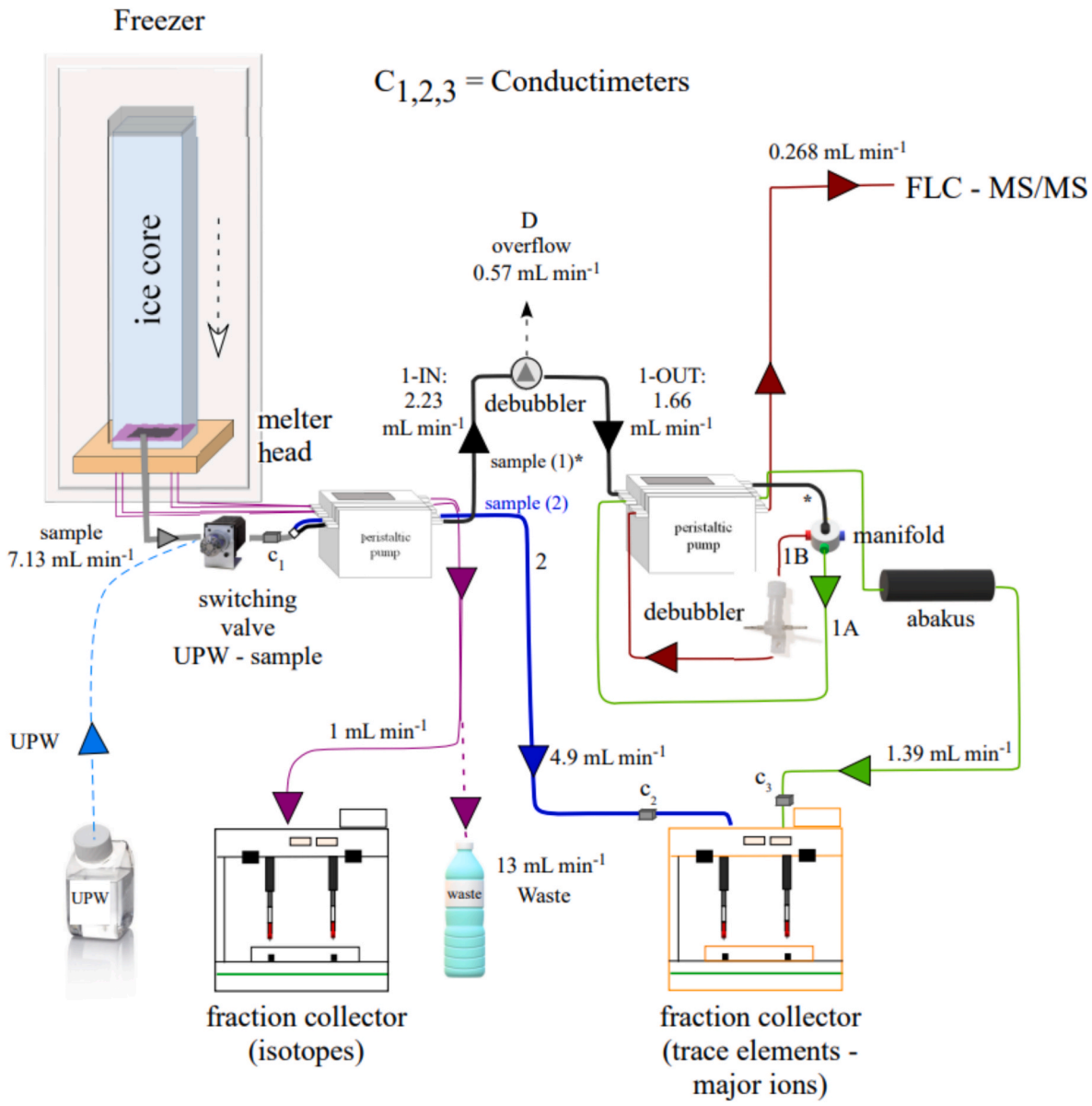

Fig. 2. Hybrid CFA system coupled with FLC-MS/MS. Asterisks in Fig. 2 indicate the part of the innermost meltwater flow which is analysed in a continuous (insoluble dust particles and conductivity) and semi-continuous manner (levoglucosan) after being split by the employed manifold. This part of the flow is distinguished from the second line of the innermost meltwater flow, which instead is directed to the fraction collector for discrete sampling.

Table 2
Description of the flow rates for the CFA – FLC system (mL min^{-1}).

Flow rates (mL min^{-1})	
Sample (grey line)	7.13
Line 1-IN (black line)	2.23
D (overflow)	0.57
Line 1-OUT (black line)	1.66
Line 1A (green line)	1.39
Line 1B (red line)	0.268
Line 2 (blue line)	4.9

(C18) (50 mm × 2.1 mm, 4 μm), Zorbax SB Aq (150 mm × 2.1 mm, 3.5 μm), and Synergi™ 2.5 μm Hydro-RP 100 Å (C18) (30 mm × 2 mm, 2.5 μm). The aim of this preliminary test was to select a column from which levoglucosan is eluted in <0.5 min, when the divert valve is switched to repeat the analysis with the second column.

The Synergy Hydro (C18) (50 mm × 2.1 mm, 4 μm) column was tested because it has been used to determine levoglucosan in other ice core studies [2], while the Zorbax SB Aq (150 mm × 2.1 mm, 3.5 μm) has been previously applied to determine the biomass mass tracer in the aerosol samples [28].. The best performances were shown using the Synergi™ 2.5 μm Hydro-RP 100 Å (C18) (30 mm × 2 mm, 2.5 μm) column. The 2.5 μm particle size of the column packing improves the efficiency (theoretical plates) of a column, producing an elution within 0.5 min with good chromatographic resolution.

Levoglucosan is a very polar hydrophilic compound and the use of methanol as an eluent in reverse chromatography causes an increase in retention time and affects the chromatographic peak width. Although methanol is the best solvent for an electrospray ionization (ESI) source [29], acetonitrile as eluent B is necessary to improve the peak symmetry of the analysed compounds (Fig. S1). We tested a first elution with 50% ultrapure water as eluent A and 50% methanol as eluent B. In the second test we used 50% acetonitrile as eluent B. The injection of 1 ng mL^{-1}, in methanol produced a peak with an average (n = 5) height of $8.2{\cdot}10^{3}\pm 5{\cdot}10^{2}$ counts, an average peak width of 0.43 ± 0.04 min and a peak asymmetry of 1.6, while the elution with acetonitrile produced a peak of

$3.2{\cdot}10^3 \pm 5{\cdot}10^2$ counts height, 0.35 ± 0.01 min wide and an asymmetry of 1.4. As previously mentioned, although acetonitrile reduces the signal height, the width and asymmetry were significantly improved. In the final optimized method, the analytes were eluted using ultrapure water produced by Elga Systems as eluent A and HiPerSolv Chromanorm acetonitrile (VWR) as eluent B.

Another important parameter that has been optimized was the column temperature since it affects the column backpressure, which is related to the solvent viscosity. As the temperature increases, viscosity decreases, and the column backpressure does the same. The back pressure can be reduced by up to 43% by increasing the temperature from 40 to 70 °C. The optimized temperature for levoglucosan analysis by FLC-MS/MS was 70 °C because an effect on the peak width is clearly showed reducing it from 0.25 min to 0.2 min with an improving of peak resolution.

The flow rate was tested between 500 and 700 μL min^{-1} (Fig. S2). Although the flow rate of 500 μL min^{-1} gave the higher peak width, and the flow rate of 700 μL min^{-1} was chosen as it resulted in a smaller uncertainty in the peak asymmetry values (close to 1).

The optimized elution program (Table 3) of column 1 at a flow rate of 0.7 mL min^{-1} follows: 0–0.4 min, 5% eluent B; 0.4−0.5 min gradient from 5 to 100%, 0.5−0.7 min, 100% eluent B (cleaning); and 0.7−1 min, equilibration with 5% eluent B. The binary elution program of the second column is the same but with a time delay of 0.5 min, so: 0.5–0.9 min, 5% eluent B; 0.9−1.0 min gradient from 5% to 100%, 1.0−1.2 min, 100% eluent B (cleaning); and 1.2−1.5 min, equilibration with 5% eluent B. The elution programs were cycled repeatedly to obtain a final run time of 40 min, the time required to analyze a 0.70 m long ice core section. The divert valve was set to switch alternately to send the flows from either the first column (i.e., 0−0.5 min) or the second column (i.e., 0.5−1 min) to the mass spectrometer.

To improve ionization in the mass spectrometer ESI source, a solution of methanol/ammonia (7‰) was added post-column at a flow of 0.07 mL min^{-1} to improve the method sensitivity.

The ESI source parameters are influenced by the mobile phase composition and its flow rate. The sources parameters were also optimized using Flow Injection Analysis (FIA). The nebulizer and auxiliary gas pressure (GS1 and GS2) were set to 50 and 60 psi, a potential of −4500 eV was applied to the source needle (IS), the source temperature was 600 °C, and the riptide gases exiting the skimmer cone (CUR), and the gas collision pressure in Q2 (CAD) were to 40 and 6 psi, respectively.

Fig. 3 reports the chromatograms of levoglucosan and internal standard obtained with the binary elution program.

3.2. Quantitative performance

Method performance was quantitatively evaluated in terms of detection and quantification limits, linear range, and reproducibility. Each standard solution was loaded into the injection-load valve located after the melting system but before the first peristaltic pump, so that each solution passed through the entire CFA system. The limit of detection (LOD) and the limit of quantification (LOQ), calculated as three and ten times the signal-to-noise ratio of known absolute amounts of the analysed target compound in a standard solution, are 66 and 200 ng L^{-1}, respectively.

The linearity was evaluated using a series of standard solutions prepared in ultrapure water with average concentrations of 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, and 50 μ g L^{-1}, with $^{13}C_6$-levoglucosan as an internal standard at a constant concentration of 1 ng mL^{-1}, directly introduced using the peristaltic pump. Considering the ratio between the levoglucosan concentration and internal standard and the ratio between the relative peak areas, we obtained R^2 value > 0.99. Instrumental precision was tested by a threefold analysis of each standard solution with 7 replicates, resulting in a relative standard deviation (RSD%) between 5 and 14% (Table 4). The higher values of RSD% were close to the LOD and below the LOQ while an RSD% < 10% was found above the LOQ.

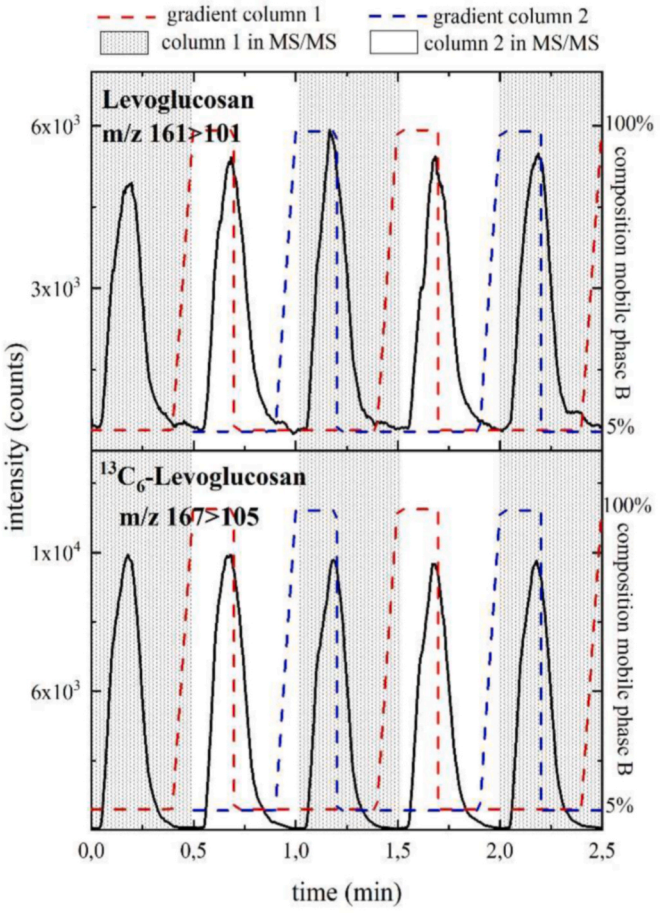

Fig. 3. Extracted ion chromatogram for each MRM transition of levoglucosan and $^{13}C_6$ levoglucosan at a concentration of 1000 ng L^{-1}. Dashed lines show the % of eluent B used in the chromatographic gradient. The cleaning and the equilibration steps start at 30 s.

Table 3
Description of the elution program for column 1 and 2.

Column 1		Column 2	
time (min)	% gradient eluent B	time (min)	% gradient eluent B
0–0.4	5	0.5–0.9	5%
0.4–0.5	5–100%	0.9–1.0	5–100%
0.5–0.7	100%	1.0–1.2	100%
0.7–1.0	equilibration 5%	1.2–1.5	equilibration 5%

Table 4
Relative standard deviation (RSD %) for the different concentration levels.

[levoglucosan]	RSD%
0.1 μg L^{-1}	14
0.2 μg L^{-1}	8
0.5 μg L^{-1}	10
1 μ g L^{-1}	10
2 μg L^{-1}	7
5 μg L^{-1}	9
10 μg L^{-1}	6
20 μg L^{-1}	5
50 μg L^{-1}	5

3.3. Method application to an ice core

The instrumental repeatability was checked by employing a pair of parallel ice sticks cut from the same ice core (GC). Concentration ranges between 0.07 and 0.84 μg L^{-1} were found for the first series of replicates, and between 0.04 and 0.83 μg L^{-1} for the second series, as shown in Fig. 4.

Considering the entire GC core, the levoglucosan signal was often below the LOD, probably due to the melting and refreezing conditions in the ice, caused by the recent warming, which might have erased the chemical fingerprints of levoglucosan, as had already occurred with major ions [27] (see Fig. 5). However, dispersed peaks were observed along the analysed profile, with the maximum signal recorded at 19.50 m of depth. Here we present the levoglucosan data for the method evaluation only, setting aside the environmental interpretation that will be addressed in future studies.

4. Conclusion

In this work we present the optimization of the CFA – FLC-MS/MS combined technique, originally developed at Ca' Foscari – CNR ISP for the analysis of vanillic and syringic acids in ice cores, and readapted here for the semi-continuous detection of levoglucosan, as a powerful marker of past fires. The proposed upgrade shows a high sensitivity, with a detection limit of 66 ng L^{-1}, which is lower than the reported LOD obtained by discrete analysis methods for alpine ice cores [26]. This is the first time that levoglucosan has been analysed in a semi-continuous manner, minimizing the sample preparation procedure, and reducing contamination problems. The analytical method has been evaluated, with linear ranges between 0.1 μg L^{-1} and 50 μ g L^{-1}, achieving an $R^2 >$ 0.99 for the linearity. Furthermore, RSD% was calculated for nine concentration values, obtaining results always lower than 10%, with the only exception of the 0.1 μg L^{-1} level, where the RSD% was equal to 14%. The robustness of the method was checked through the analysis of a shallow ice core drilled at the Grand Combin glacier, which required to run the system for several hours. Additionally, the instrumental repeatability was verified through the employment of pairs of parallel ice sticks, where the concentration trends should be similar. Our findings demonstrate the value of levoglucosan determination within alpine ice cores by employing the coupled CFA – FLC-MS/MS technology, after an accurate chromatographic and spectrometry optimization.

Credit author statement

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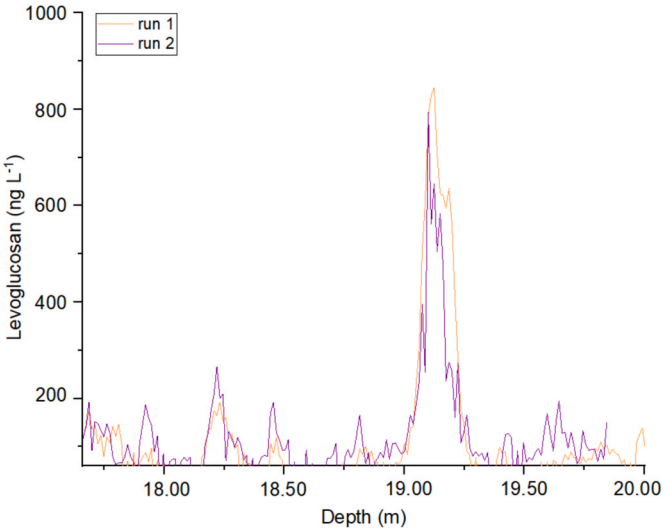

Fig. 4. Reproducibility of levoglucosan profiles along the GC ice core: from 17.66 m to 20.09 m of depth (bag 32 to bag 35: orange; bag 32 bis to bag 35 bis: blue).

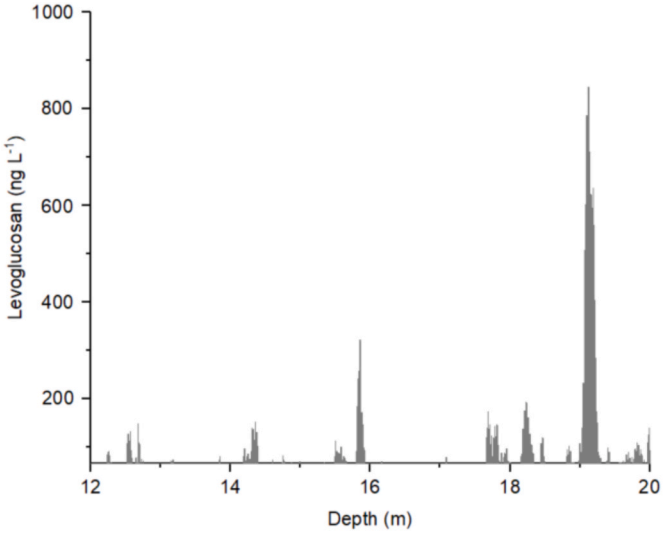

Fig. 5. Levoglucosan profile (ng L^{-1}) along the ice core (depth from the surface).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2023.124799.

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