ANNALS OF GEOPHYSICS, 67, 4, GC442, 2024; doi:10.4401/ag-9131
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# Review of recent advances in Continuous Flow Analysis (CFA) technique for polar and alpine ice cores

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Article history: received July 25, 2024; accepted September 11, 2024

## Abstract

Continuous Flow Analysis (CFA) systems, originally designed for field analyses of trace chemical species in ice cores, have seen significant innovations over the past decade, particularly through the integration of new spectrometric (Inductively Coupled Plasma Mass Spectrometers, Laser Absorption Spectrometers) and chromatographic techniques (Ionic Chromatography, Gas Chromatography and Liquid Chromatography). This paper reviews recent technical and methodological advances in CFA adopted by leading laboratories worldwide for the high-resolution detection of trace elements, major ions, isotopic and gaseous species, and insoluble particles in polar and alpine ice cores, exploring the strengths and limitations of different couplings, and discussing potential future enhancements.

Keywords: Continuous Flow Analysis; Ice Cores; Innovation; Chromatographic techniques; Spectrometric techniques

## 1. Introduction

Ice cores are one of the best resolved paleoclimate archives, and the unique which preserve information on both climate forcings (e.g., Greenhouse Gases, GHG) and responses (e.g., temperature variations) (Steig, 2008). They offer a valuable opportunity to investigate past changes in atmospheric composition and regional-to-synoptic circulation patterns through the analysis of dissolved, particulate matter, and gaseous species, respectively trapped in ice crystals and air bubbles during wet and dry deposition (Thompson et al., 2005; Jouzel and Masson-Delmotte, 2010, and reference therein). However, for long time, ensuring contamination-free analytical methods that preserve trace-level concentrations (ppb, ppt) of impurities in ice cores while achieving a high vertical sampling resolution of approximately one sample per centimetre has been one of the primary challenges faced by paleoclimate working groups (Breton et al., 2012).

Continuous ice core melter systems, which allow for the collection of discrete samples and Continuous Flow Analysis (CFA) of meltwater, channelled from the inner portion of the ice core sample, meet these requirements, and overcome the labour-intensive sample preparation that limits the traditional analytical method (Breton et al., 2012; Erhardt et al., 2019). CFA was introduced in the early 1990s, originally designed for field analyses of trace chemical species, such as hydrogen peroxide ($H_2O_2$), formaldehyde (HCHO), ammonium ($NH_4^+$), and calcium ($Ca^{2+}$) in ice cores (Sigg et al., 1994). The benefits of this approach, represented by ultra-high resolution in depth (age) domain, reduced time effort in ice cores processing, limited risk of contamination, and applicability to any species for which there is a sensitive continuous analysis method, caught the interest of paleoclimatic community, leading to significant methodological advances over the past 20 years (e.g., Röthlisberger et al., 2000; McConnell et al., 2002; Knüsel et al., 2003; Osterberg et al., 2006; Traversi et al., 2007; Kaufmann et al., 2008; Schüpbach et al., 2009; Bigler et al., 2011; Chappelaz et al., 2013; Dallmayr et al., 2016; Grieman et al., 2022; Barbaro et al., 2022). Today, the CFA is a method deployed worldwide, with different modifications of the experimental setup implemented in leading research laboratories dealing with the ice cores and paleoclimate studies, to precisely resolve the chemical composition of compressed ice layers of deep-drilled ice cores, especially from polar regions. From the early 2000s, paleoclimatic studies evolved towards the coupling of CFA systems with chromatographic techniques, achieving higher sensitivity and higher throughputs thanks to the advantages of continuous melting systems combined with the accuracy, precision, and low detection limits of chromatographic methods coupled with conductimetry or mass spectrometry (Udisti et al., 2000; Huber et al., 2001; Traversi et al., 2002; Morganti et al., 2007), with notable advancements achieved during the last decade (Severi et al., 2015; Ro et al., 2020; Barbaro et al., 2022; Spagnesi et al., 2023a). Concurrently, significant efforts were dedicated to improve CFA techniques for elemental, isotopic, and gaseous species detection in polar and alpine ice cores, through the coupling of CFA systems with Quadrupole Mass (QMS), Sector Field Mass (SFMS), Time-Of-Flight (TOF), Cavity Ring-Down (CRDS), Off-Axis Integrated Cavity Output (OA-ICOS), and Optical Feedback – Cavity Enhanced Absorption (OF-CEAS) spectrometers (e.g., McConnell et al., 2002; Schüpbach et al., 2009; Chappelaz et al., 2013; Emanuelsson et al., 2015; Rhods et al., 2015; Arienzo et al., 2019; Erhardt et al., 2019; Grieman et al., 2022; Song, 2023). Chemiluminescence (CL) has also been incorporated into CFA systems for detecting $Fe^{2+}$ (a volcanic proxy) in ice cores, replacing the previously used absorption spectrometry and spectrophotometric techniques (Burgay et al., 2019, and reference therein). Moreover, laser-based instruments such as the Abakus particle counter for high-resolution detection of insoluble particles, and the Single Particle Soot Photometer (SP2) for quantifying black carbon in ice cores, have been integrated into continuous flow systems.

This review provides a comprehensive assessment of existing literature on CFA systems coupled with chromatographic and spectrometric techniques for applications to polar and alpine ice cores, with a special focus reserved for developments presented in the last decadal literature. Additionally, a concise overview of chemiluminescence and laser-based techniques for insoluble particles detection is presented. The techniques areas for improvement are thus explored, addressing outstanding issues raised in a recent review by Du et al. (2018): i) Uncertainties arising from the random distribution of impurities and air bubbles during constant melting (Wu et al., 2004; 2009), ii) Memory effect between samples, iii) Mixing effect, iv) The balance between high sampling resolution, rapid handling, and minimal sample mixing, and v) Discrepancies between continuous sampling and discrete analysis. In addition, future perspectives for CFA systems are also discussed.

# 2. Continuous Flow Analysis (CFA) coupled systems

## 2.1 Chromatographic techniques deployed within CFA systems

The first couplings between Continuous Flow Analysis (CFA) systems and chromatographic techniques date back to the early 2000s, with the pilot employment of Fast Ion Chromatography (FIC) for quantitatively detect chloride ($Cl^-$), nitrate ($NO_3^-$), and sulphate ($SO_4^{2-}$) in ice (Udisti et al., 2000). Later, gradual improvements in temporal resolution and chromatographic efficiency were achieved, ranging from systems capable to conduct one measurement per minute, yielding a spatial resolution of 4 cm (Traversi et al., 2002), to depth resolutions of 2 cm, obtained with a sampling frequency of 1.33 minutes per measurement (Cole-Dai et al., 2006). In the same years, a Gas Chromatography – Flame Ionization Detector (GC – FID) was first incorporated in a CFA system for semicontinuous and field-deployable measurements of methane ($CH_4$) in ice cores (Schüpbach et al., 2009). This technique was successfully applied on a section of the ice core from Talos Dome (Antarctica) (Urbini et al., 2008), obtaining a depth resolution of 12-15 cm, correspondent to a measurement every 3.5 min, at the chosen melt rate of 3.5 cm min$^{-1}$. Good agreement between CFA-$CH_4$ raw data and the data points measured by the wet extraction method was demonstrated, thus the feasibility of the new technique, despite further necessary calibrations of the $CH_4$ data to overcome possible overestimates (Kr calibrations), and underestimates ($N_2$+$O_2$ calibrations) of the $CH_4$ concentration with respect to wet extraction $CH_4$ data. Indeed, assuming that the water for the standard measurements still contained a considerable amount of air, the higher solubility of Kr in water compared to $CH_4$, and of $CH_4$ compared to $N_2$, would explain the overestimation of $CH_4$ concentration using Kr, and the underestimation using $N_2$+$O_2$ in the sample measurements (Schüpbach et al., 2009).

### 2.1.1 Technical and methodological advances in CFA – Chromatography couplings

The most significant advancements in chromatographic techniques combined with continuous flow systems began in the 2010s, with the introduction of the Ultra-FIC method (Severi et al., 2015). This innovative approach, tailored for achieving high resolution of $SO_4^{2-}$ profiles crucial for stratigraphic dating of polar ice cores, enabled a depth resolution of 1.0 cm and an IC sampling frequency of 30 s by combining two parallel IC sets. Widely employed for analyzing extensive sections of the deep EPICA Dronning Maud Land (EDML) ice core drilled in Antarctica, this method effectively doubled the resolution of $SO_4^{2-}$ compared to traditional IC techniques. However, the Ultra-FIC method faced limitations with respect to the FIC, in accurately determining $Cl^-$ due to insufficient separation between the $Cl^-$ peak and the water dip, requiring a double loading time of sample to 30 s for each IC to address this issue, at the expense of reducing the depth resolution to 2.0 cm (Severi et al., 2015). To improve the typically limited depth resolution of continuous IC during simultaneous analysis of cations and anions, caused by the large volume of meltwater required per analyzed sample (Huber et al., 2001; Cole-Dai et al., 2006; Morganti et al., 2007; Severi et al., 2015), a system of six sequential ion chromatograph detectors was designed to create a multi-IC setup for consecutive online measurements (Ro et al., 2020). Initially suggested by Cole-Dai et al. (2006), this method proved effective in providing high-resolution ion data for reconstruction rapid environmental changes, but improvable in providing sufficient baseline separation between $CO_3^{2-}$ and $SO_4^{2-}$, and in lowering the Method Detection Limits (MDLs) for $SO_4^{2-}$ below the measured 3 µg L$^{-1}$ (Ro et al., 2020).

The necessary improvements to overcome the limitations of the FIC were achieved with a novel coupling between melter system and Fast Liquid Chromatography tandem Mass Spectrometry (FLC – MS/MS) (Barbaro et al., 2022). This instrumental combination guarantees 1 measurement every 30 s, which corresponds to a sampling resolution of 1.5 cm with a melting rate of 3.0 cm min$^{-1}$. Although designed for analyzing specific biomass burning tracers (i.e., Vanillic, VA, and Syringic, SyA, acids) trapped within the ice, this technique can be used to determine any organic compound after optimization of the chromatographic and mass spectrometric parameters, while FIC is limited to the determination of ions. The innermost meltwater flow channeled to FLC system was reduced to 268 µL min$^{-1}$, optimized to completely fill the two loops of 100 µL of volume each, with a loss of 0.35 cm between FLC measurements, compared to the depth interval loss of 1.42 cm between FIC measurements (Grieman et al., 2022). Furthermore, an upgrade of the innovative CFA – FLC – MS/MS coupling was recently provided by Spagnesi et al., 2023a), with an optimized system 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 sampling resolution down to 1 cm, and 0.23 cm of depth interval lost, with a melting rate reduced from 3 to 2 cm min$^{-1}$. This novel setup allowed to achieve higher sensitivity and lower limit of detection (LOD) 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$^{-1}$ (Legrand et al., 2007). Recent advancements in coupled techniques involving chromatographic and continuous flow systems have thus significantly improved analytical conditions (flow rate, sensitivity, sample loss, depth resolution), and expanded the number of chemical species that can be analyzed in ice cores, as summarized in Table 1.

## 2.2 Spectrometric techniques deployed within CFA systems

Since the early 2000s, the integration of various spectrometric techniques with continuous flow systems has revolutionized ice core science, offering a wide range of applications. Initially, mass spectrometric techniques, which analyze the mass-to-charge ratio of ions to identify molecules and their quantities, were combined with melter

| Best analytical conditions | FIC, Ultra-FIC, Multi-IC | FLC – MS/MS |
|---|---|---|
| Min melting rate (cm $min^{-1}$) | 1.5 | 2 |
| Max depth resolution (cm) | 1 | < 1 |
| Max sampling frequency (min) | 0.5 | 0.5 |
| Min flow rate (mL $min^{-1}$) | 1 | 0.26 |
| Max sample loss (cm) | 1.42 | 0.23 |
| Chemical species detectable | only ions | organic tracers, ions |

**Table 1.** Best analytical conditions achieved by FIC, Ultra-FIC, multi-IC and FLC – MS/MS techniques recently coupled with Continuous Flow Analysis systems.

systems to achieve continuous concentration records of elements and chemical species in ice cores at parts per billion (ppb) and parts per trillion (ppt) levels (McConnell et al., 2002; Knüsel et al., 2003). This combination, now a standard practice, include the melting and subsequent acidification of meltwater with diluted ultrapure acid ($HNO_3$ 1-2%) to dissolve particles prior to injection into the Inductively Coupled Plasma – Mass Spectrometer (ICP – MS). This approach significantly reduced sample handling by CFA, which directly inject the decontaminated meltwater stream into the analytical instruments within a few minutes, ensuring consistency in acidification amount and time, and high-depth-resolution measurements (~ 5 to 30 mm). Subsequently, Laser Absorption Spectrometers (LAS) (Crosson, 2008), capable of quantifying element concentrations by measuring the absorption of specific wavelengths of light, were interfaced with continuous flow systems to continuously measure stable hydrogen δD ($\delta^2H$) and oxygen ($\delta^{18}O$) isotope ratios in ice cores (Gkinis et al., 2010). This involved employing both Wavelength Scanned – Cavity Ring-Down Spectroscopy (WS-CRDS) and Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) LAS techniques. Notably, the precision of hydrogen and oxygen isotope measurements with WS-CRDS was found to be comparable to the previously utilized Isotope-Ratio Mass Spectrometry (IRMS) Gkinis et al., 2011; Maselli et al., 2013), leading to WS-CRDS being extensively adopted in combination with CFA as a cost-effective and time-efficient alternative to IRMS. Concurrently, the first introduction of Optical Feedback Cavity Enhanced Absorption Spectroscopy (OF-CEAS) marked a milestone, as its deployment in polar field settings interfaced with Continuous Flow Analysis systems provided continuous methane ($CH_4$) records, further expanding the scope of ice core research (Chappellaz et al., 2013).

### 2.2.1 Technical and methodological advances in CFA – Spectrometry couplings

The integration of atomic spectroscopy and mass spectrometry with CFA systems has significantly expanded the range of measurable analytes in polar and alpine ice. The ICP instruments typically coupled to CFA system are Quadrupole Mass Spectrometry (QMS) and Sector Field Mass analyzers (SFMS). SFMS, distinguished by its higher mass-resolving power and sensitivity compared to QMS, has emerged as the preferred option for analytical applications demanding exceptional resolution, sensitivity, and accuracy (e.g., Uglietti et al., 2014, and reference therein; Vallelonga et al., 2021). However, both analyzers are capable to measure only a single mass at any given time without losing sensitivity, thereby limiting the number of elements that can be quantified quasi-simultaneously. To address this drawback, a sensitive Time-Of-Flight Mass Spectrometer (TOFMS), became recently available for ICP ion sources (Borovinskaya et al., 2013), was interfaced with a continuous melting system (Erhardt et al., 2019; Erhardt et al., 2023). The TOFMS was equipped with a quadrupole notch filter used to attenuate high-intensity spectral peaks, reduce signal background, and protect its detector. This novel coupling demonstrated the capability of icpTOF to overcome the instrumental limitations of scanning mass analyzers by measuring all analyte masses at virtually the same time, detecting multi-elemental fast transient signals, and ensuring higher time resolution than established methods. This is particularly crucial for thinned ice core samples, where the detection of annual layer signals is hampered by low-sensitive measurement techniques. Indeed, low sensitivity techniques may not detect very low concentrations, which are often critical for identifying annual layers. Furthermore, in low sensitivity measurements, the signal from the sample can be overwhelmed by background noise, making it difficult to identify small variations that correspond to annual layers. Additionally, while coupled techniques in continuous flow systems significantly enhance detection capabilities, they also generate big quantities of data. This can make data processing complex, requiring advanced computational tools and methods to manage and interpret the extensive datasets effectively.

Despite recent advances achieved, when evaluating the continuous measured concentration of elemental impurities in ice core samples performed with spectrometric techniques coupled to CFA systems, a thorough methodological assessment is imperative. Indeed, despite the advantages of continuous measurements, very limited leaching times (a few minutes) are allowed with CFA-ICP-MS integrated systems, in contrast to days to months possible in discrete analyses, thus resulting in under-recovery of several elements. Therefore, adjusting final concentrations based on discrete sample analyses conducted at least three months after acidification, as suggested by Arienzo et al. (2019), would be beneficial. It has been showed indeed that sodium (Na), strontium (Sr), and sulphur (S) dissolve readily and can be fully recovered during continuous measurements. In contrast, the average recovery for other elements can vary: 70-100% for cadmium (Cd), gadolinium (Gd), magnesium (Mg), manganese (Mn), uranium (U), and ytterbium (Yb); 50-90% for calcium (Ca), cerium (Ce), samarium (Sm), and vanadium (V); and less than 50% for aluminum (Al), iron (Fe), and lanthanum (La). However, this is not a common practice due to logistical challenges such as increased time effort, larger volumes of data produced, and the need for significant storage space for discrete samples collected.

Over the last decade, significant progress was also made by coupling CFA systems with new-generation OA-ICOS and WS-CRDS spectrometric techniques, enabling routine high-resolution measurements of water stable isotopes in ice cores. Emanuelsson et al. (2015) compared CFA setups coupled with OA-ICOS and WS-CRDS, deployed in a system developed to continuously analyze the Roosevelt Island Climate Evolution (RICE) Antarctic ice core, and found that each method had its advantages and disadvantages, depending on the analytical requirements. Notably, OA-ICOS, which directly measures absorption, provided accurate measurements at very high concentrations, while WS-CRDS was effective if the ringdown time was sufficiently long. However, for analyzing secondary parameters such as d-excess and $^{17}$O-excess, a system optimized for stability, like the CRDS setup, had an advantage over OA-ICOS analyzers, which are more influenced by instrumental drift (with $\delta^{18}$O being more drift-sensitive than $\delta$D), as previously suggested also by Aemisegger et al. (2012). Consequently, WS-CRDS became more frequently employed in combination with CFA systems, allowing for improved data density and sample throughputs (Jones et al., 2017). A significant methodological breakthrough was then achieved with the use of two WS-CRDS instruments simultaneously coupled with a continuous flow system, enabling concurrent measurements of $\delta$D, $\delta^{18}$O, and $\delta^{17}$O, along with the “excess” parameters d, $d_{ln}$, and $\Delta^{17}$O (Steig et al., 2021). Once applied to a South Pole ice core as an example, this setup facilitated the production of a comprehensive 54,000-year record of $\delta$D, $\delta^{18}$O, d and $d_{ln}$ with a resolution of 0.5 cm for $\delta$D, $\delta^{18}$O, and $\delta^{17}$O, and an approximately 50,000-year record of $\delta^{17}$O and $\Delta^{17}$O. Indeed, precise continuous measurements of $\delta^{17}$O using laser spectroscopy have been shown to be as straightforward as those for $\delta$D and $\delta^{18}$O, yielding results competitive with discrete laser or IRMS measurements (Davidge et al., 2022). However, to achieve a complete and continuous vaporization for reducing errors in all WS-CRDS stable water isotope measurements, and especially for attaining the per-meg precision necessary to detect meaningful variations in $\Delta^{17}$O, a custom vaporizer was needed. This unit, recently realized to achieve a short retention time within the vaporizer that limits the mixing of adjacent ice core layers, particularly benefits from both a small volume of the flash vaporizer and from the production of excess sample vapor (Davidge et al., 2022). Further advancement in water stable isotope analysis, potentially applicable to continuous flow systems, has been achieved with the development of a standalone water vapor generation module designed for high-precision liquid water isotope measurements with WS-CRDS (Steen-Larsen and Zannoni, 2024), enabling seamless switching between water sources, supporting calibration with multiple standards, and offering a broad humidity generation range (from 300 to 30,000 ppmv).

Commercially available WS-CRDS technologies have also been shown to be suitable for continuous high-resolution analysis of gaseous species like $CH_4$ in ice cores, following specific modifications to stabilize cavity pressure (Stowasser et al., 2012). Indeed, when the sample gas flows are adjusted to match the melt speed of the

| Spectrometric techniques deployed within CFA systems | Type of Analysis | Strengths | Limits | References |
|---|---|---|---|---|
| ICP-QMS (Inductively Coupled Plasma-Quadrupole Mass Spectrometer) | Elemental (ppb or ppt level) | High mass resolving power, high sensitivity | Single mass measurement at any given time; elemental under-recovery due to limited acidification time (few min) | McConnell et al., 2002; Arienzo et al., 2019 |
| ICP-SFMS (Inductively Coupled Plasma-Sector Field Mass Spectrometer) | Elemental (ppt level) | Higher mass resolving power and higher sensitivity than ICP-QMS | Single mass measurement at any given time; elemental under-recovery due to limited acidification time (few min) | McConnell et al., 2002; Knüsel et al., 2003 |
| ICP-TOF (Inductively Coupled Plasma-Time-Of-Flight) | Multi-elemental (ppb or ppt level) | Measure all analyte masses at the same time; multi-elemental detection of fast transient signal; higher time resolution than ICP-QMS and ICP-SFMS | Detection limits can be lower than ICP-SFMS for certain ultra-trace elements; difficulties in resolving isobaric interferences; lower sensitivity than ICP-SFMS | Erhardt et al., 2019; Burgay et al., 2019 |
| OA-ICOS (Off-Axis Integrated Cavity Output Spectroscopy) | Water stable isotopes | High resolution measurements | Susceptibility to drifts for $\delta^{18}O$ | Emanuelsson et al., 2015 |
| WS-CRDS (Wavelength Scanned-Cavity Ring-Down Spectroscopy) | Water stable isotopes; $CH_4$ | High resolution measurements, competitive with IRMS methods | Resolution can be affected by dispersion and memory effects if pressure and internal volume are not adequately reduced | Gkinis et al., 2010, 2011;<br>Stowasser et al., 2012;<br>Emanuelsson et al., 2015;<br>Jones et al., 2017b;<br>Steig et al., 2021;<br>Davidge et al., 2022 |
| OF-CEAS (Optical Feedback-Cavity Enhanced Absorption Spectroscopy) | CO, $CH_4$ and $H_2O$ | High frequency of acquisition;<br>high resolution;<br>low detection limits | Complex, expensive instrumentation; interferences when multiple gases have overlapping absorption lines | Chappellaz et al., 2013; Rhodes et al., 2013, 2015; Faïn et al., 2014; Song, 2023 |

**Table 2.** Overview of uses, strengths and limits of different spectrometric techniques coupled with CFA systems.

CFA system, reducing from the original 70-400 mL min$^{-1}$ to the typical melting flow of 1-1.5 mL min$^{-1}$, the cavity pressure becomes unstable, invalidating the measurements. To address this, Stowasser et al. (2012) recommended replacing the orifice at the WS-CRDS inlet with a fused silica capillary to increase inlet gas flow resistance, and placing a needle valve between the proportional control valve at the cavity outlet and the diaphragm pump to adjust the pump rate. Additionally, to improve resolution affected by dispersion and memory effects, it was suggested to both reduce the pressure in the sample cavity from 225 mbar to 60 mbar, and the internal volume of the WS-CRDS by switching to small-diameter tubing throughout the spectrometer. However, while lowering the sample pressure enhances resolution, it decreases the precision due to a smaller signal-to-noise ratio, necessitating a compromise between resolution and precision for each application. Despite these adjustments, WS-CRDS has not been further employed for continuous $CH_4$ detection in ice cores since the incorporation of Optical Feedback Cavity Enhanced Absorption Spectroscopy (OF-CEAS) into existing CFA systems (Song, 2023 and reference therein). Unlike WS-CRDS, which measures ring-down time, OF-CEAS relies on quantifying light transmission through a high-finesse optical cavity at specific wavelengths. This technique, adopted by SARA laser spectrometers (Spectroscopy by Amplified Resonant Absorption, developed at Laboratoire Interdisciplinaire de Physique, Grenoble), ensures a higher frequency of acquisition of the absorption spectrum by the sample in the cavity. Specifically, OF-CEAS can resolve periodic input signals with frequencies below $0.01 s^{-1}$ and can be used with a continuous melting system to measure CO, $CH_4$, and $H_2O$, fitting the sample gas absorption spectrum in the 2325.1-2325.5 nm wavelength range at a rate of 6 Hz (Chappellaz et al., 2013; Rhodes et al., 2013; Faïn et al., 2014; Rhodes et al., 2015).

A comprehensive comparison of uses, strengths and limits of different spectrometric techniques deployed within CFA systems is summarized in Table 2.

## 2.3 Chemiluminescence deployed within a CFA system

The scalability of continuous melting systems allows their interface with any sensitive continuous flow method, in addition to the aforementioned spectrometric and chromatographic techniques, provided the competing demands of different instrumentation can be respected. For instance, chemiluminescence was recently coupled to the Bern Continuous Flow Analysis system (CFA-CL) for the determination of $Fe^{2+}$ species in ice cores, demonstrating low detection limit, high sensitivity, high accuracy, and good precision, as well as higher response and lower memory effects when linked to CFA, with respect to absorption spectrometry methods previously adopted (Spolaor et al., 2012b, 2013a; Hiscock et al., 2013). All these features indicated that this technique might be particularly suitable for deep ice cores analyses where the low sample availability requires high-resolution techniques (Burgay et al., 2019).

## 2.4 Laser-based techniques coupled with CFA systems

In addition to traditional methods for analyzing chemical species in ice cores, laser-based techniques have been successfully integrated into CFA systems, significantly improving the detection of insoluble particles. A prime example is the Abakus microparticles detector, a laser-based device that measures optical transmissivity through a laser beam within a flow cell continuously filled with sample flow (Kaufmann et al., 2008). This instrument was first introduced during the 2000 North Greenland Ice Core Project (NorthGRIP) to provide continuous measurements of microparticle concentration and size distribution in the range from 0.8 μm to 15 μm, adjustable across 32 bins (Ruth et al., 2002). Its low maintenance needs during CFA operation, minimal sensitivity to electrical noise (Simonsen et al., 2018), and compatibility with continuous flow systems have contributed to its widespread adoption (e.g., Bigler et al., 2011; Erhardt et al., 2019; Ro et al., 2020; Nagatsuka et al., 2021; Grieman et al., 2022; Spagnesi et al., 2023a; Hudak et al., 2024).

In parallel, the Single Particle Soot Photometer (SP2) – a laser-induced incandescence instrument designed to measure the refractory black carbon (rBC) mass in individual particles regardless of their morphology or coatings with light-scattering material (Baumgardner et al., 2004; Schwarz et al., 2006) – started to be adopted for ice core analysis, replacing previously used thermal-optical methods (e.g., Kaspari et al., 2011, and reference therein). This technique, first described by Stephens et al. (2003), involves heating light-absorbing refractory aerosol to vaporization with an intense laser beam, causing them to emit visible thermal radiation that reveals the particle's composition and mass (Schwarz et al., 2006). The SP2 was first applied at the Desert Research Institute (DRI) in Reno, Nevada, USA (McConnell et al., 2007), and quickly became a standard part of DRI's instrumentation suite (McConnell et al., 2021). Subsequently, an enhanced technique was developed to analyze rBC concentration in ice cores by modifying the SP2 to extend the detectable size range of BC particles. This adaptation allows for the detection of BC particles with diameters ranging from 70 nm to 4 μm, compared to the standard SP2's range of 70 and 850-900 nm (Moteki and Kondo, 2010). The advanced device, equipped with a high-efficiency concentric pneumatic nebulizer (Marin-5, Teledyne CETAC, USA), was developed by Mori et al. (2016) and recently adopted by Goto-Azuma et al. (2024).

## 3. Discussion

Since their initial design for field deployment at the University of Bern (Sigg et al., 1994), CFA systems have undergone significant improvements, enhancing their capability to analyze impurities, particles, and gaseous species within ice cores using compact, modular, robust, and transportable setups. Notable early advancements in the stabilization and utilization of melting samples within CFA systems were made at the University of Bern, Switzerland (UBern-CFA, Kaufmann et al., 2008; Erhardt et al., 2019). Other major improvements were developed at several notable institutions: the University of Copenhagen, Denmark (CIC-CFA, Bigler et al., 2011; Emanuelsson et al., 2015; Kjær et al., 2016), the Institute of Environmental Geosciences in Grenoble, France IGE-CFA, Chappellaz et al., 2013; Rhodes et al., 2013, 2015), the Desert Research Institute in Reno, Nevada, USA (DRI-CFA, Arienzo et al., 2019), the National Institute of Polar Research (NIPR) in Tokyo, Japan (NIPR-CFA, Dallmayr et al., 2016), the British Antarctic Survey in Cambridge, UK (BAS-CFA, Grieman et al., 2022), the Korea Polar Research Institute (KOPRI) in Incheon, South Korea (KOPRI-CFA, Ro et al., 2020), and the University of Venice, Italy (ISP/UNIVE-CFA, Barbaro et al., 2022; Spagnesi et al., 2023a). Each system is characterized by peculiar components of the analysis unit, aligned to the needs of the various laboratories. An overview of those peculiarities for the major CFA systems is illustrated in Fig. 1.

Despite significant advances in CFA technique that have enabled successful applications, several issues remain to be carefully addressed. These include sample memory, mixing effects, uncertainties from the random distribution of impurities and air bubbles during continuous melting, and discrepancies between continuous sampling and discrete analysis. Moreover, the quantification and lowering of Limits of Detection (LODs), particularly for trace element analysis, as well as the reduction of sample contamination, which may arise from various sources, are persistent challenges that must be addressed when working with continuous flow systems. Additionally, the CFA technique

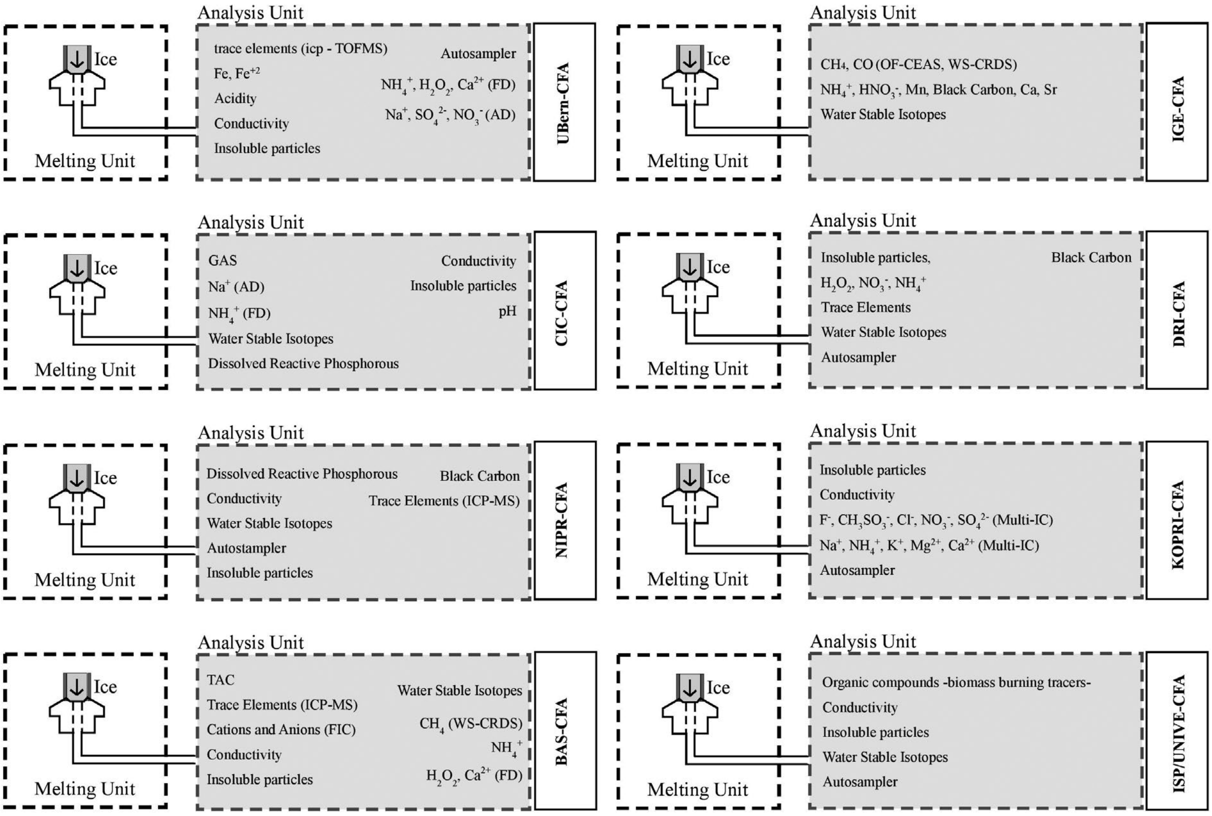

**Figure 1.** Overview of recent advances in CFA systems implemented at prominent institutions: University of Bern (Ubern), University of Copenhagen (Ucopenhagen), National Institute of Polar Research (NIPR), British Antarctic Survey (BAS), Institute of Environmental Geosciences (IGE), Desert Research Institute (DRI), Korea Polar Research Institute (KOPRI), Institute of Polar Sciences/Ca' Foscari University of Venice (ISP/UNIVE). The term "GAS" refers to extraction lines for unspecified gaseous species. "FD" and "AD" denote fluorometric and absorption detection, respectively. "Va" and "SyA" stand for vanillic and syringic acids, respectively.

has long been deemed unsuitable for ice cores from non-polar regions due to high particle levels, and pre-injection filtration required (Du et al., 2018). However, recent approaches have been proposed to address these challenges.

To limit signal dispersion and improve depth resolution, strategies include shortening the lengths of tubing between the melt head and instruments, reducing the melt rate to the minimum necessary for feeding all connected instruments (Grieman et al., 2022), and removing air from the sample stream as late as possible in the path from the melt head to a mass spectrometer analyzer (Erhardt et al., 2019). While memory and mixing effects cannot be entirely avoided, thoughtful design choices can help reduce them. Increasing the flow velocity during ice core analysis and minimizing tubing diameters can lead to shorter retention times and reduced system mixing. Conditioning the system with at least 10 min of water with similar isotopic composition before analysis can limit isotopic system memory between samples, preventing mixing between isotopically disparate reference waters and ice core samples (Davidge et al., 2022). Furthermore, the transfer function, which represents the system's response to an instantaneous isotopic change at the melt head or stream selection valve, and the impulse response function defined using mock ice or laboratory water standards, can be employed to characterize mixing. The mixing length corresponds to the standard deviation of the impulse response function, which is the first derivative of the transfer function (Gkinis et al., 2011; Jones et al., 2017). For $CH_4$ measurements, long uninterrupted periods of melting are required to limit dispersion and memory effects (Emanuelsson et al., 2015). Additionally, lowering cavity pressure and reducing volume in the spectrometer can decrease sample gas dispersion and memory effects (Stowasser et al., 2012). Furthermore, to resolve discrepancies between continuous sampling and discrete analysis of elemental concentrations in ice, it would be recommended to compare their results and adjust continuous measurements based on discrete sample analysis at least three months after acidification. This timing is crucial because the shorter acidification time (few min) during Continuous Flow Analysis may lead to a measured elemental concentration that is lower than that obtained through discrete analysis (Arienzo et al., 2019).

Reducing and quantifying LODs for analyzed species, and especially for trace elements, is also a critical factor to be addressed in assessing the sensitivity and reliability of the CFA technique. LODs in CFA can be mostly influenced by instrumental constraints such as instrument sensitivity, detection technology, and signal-to-noise ratio, as well as by not strict quality control measures nor optimized setup conditions. For example, factors like rapid flow rates may compromise sensitivity, resulting in higher LODs.

Furthermore, the accuracy of results can be compromised by contamination issues stemming from various sources, despite the use of high-purity melt head materials and/or coatings, as well as differential pump rates that ensure that contamination on the external surface of the ice is not able to mix with the meltwater at the centre of the melter (Spolaor et al., 2012a). Specifically, contamination can occur during sample handling, such as cutting and preparation of ice core sections, including contamination from tools, surfaces, laboratory environment, and human contact. Additionally, inadequately maintained pump systems, tubing, and connector can lead to systematic contamination. Analytical instruments may also contribute to contamination if contaminants enter the detection system. Moreover, in continuous flow systems, there is a risk of cross-contamination between consecutive samples, which can be mitigated through proper design of the sample introduction system and through flushing with Ultra Pure Water (UPW) between samples. However, the latter approach can have a negative impact on water stable isotopes analysis because of the large isotopic difference between UPW and samples. To address these contamination challenges effectively, it is imperative to implement stringent protocols, including employing high-purity reagents and materials, regularly cleaning and calibrating equipment, implementing rigorous quality control on blank samples and standards, and providing comprehensive training for personnel handling the ice cores.

The CFA technique has proven to be suitable for ice cores from non-polar regions, if certain measures are taken. Recommended precautions include excluding layers with visible debris concentration, typically found at the bottom of ice cores, which can be pre-filtered and analyzed discretely. Additionally, filters should be inserted upstream of the instrumentation to be removed and cleaned after each run. A second low-volume debubbler should be added downstream of the pumps to maintain a minimum buffer and prevent disruptions from high concentrations of air bubbles released during melting. Moreover, the melt head should be cleaned frequently (Spagnesi et al., 2023b).

## 4. Conclusions and perspectives

Since 2000, Continuous Flow Analysis has risen as a pivotal technique in ice core research, although long perceived as applicable solely to polar samples due to their sparse particle content. The continuous flow technique offers crucial advantages, which include high-resolution measurements of dissolved, particulate, and gaseous species in ice cores, reduced preprocessing and analysis time efforts, and minimized contamination risks due to reduced sample handling. The modularity and versatility of the system has allowed important advances in the last two decades, expanding the number of chemical species that can be analyzed, and declining its employment in increasingly advanced configurations. In addition, the ability to simultaneously collect discrete samples during continuous measurements has enhanced the robustness of this technique, while broadening its analytical scope.

However, this technique still has potential for enhancement, particularly in the areas of automation and process optimization. For example, since the extraction and classification of climate-relevant ice core particles (mineral dust, tephra, pollens) is extremely laborious, and the employable optical systems (i.e. laser-based Klotz Abakus sensor) in a CFA workflow are insensitive to the type of particle entering the detector, the deployment of a deep neural networks-based system, like the one presented by Maffezzoli et al. (2023), could help to achieve autonomous and simultaneous detection. Additionally, the gas extraction line implemented within some CFA systems, could be adapted to allow the collection of discrete samples of gases to be analyzed off-line for $^{39}$Ar, a noble gas radioisotope through which investigate the range of 50-1000 years, and dating alpine ice cores (Feng et al., 2019). Moreover, large volume of data produced by continuous flow systems requires robust infrastructures that may be implemented to accumulate, store, and manage them efficiently, ensuring that post-processing tasks are handled smoothly and effectively. Therefore, greater efforts would be desirable in the near future also in this field.

Although CFA remains the most comprehensive and rapid approach in ice core science, its results can be potentially augmented by applying Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS) technique to discrete samples. Indeed, to achieve higher resolution trace element characterization along ice cores, often down to a few micrometers, LA-ICP-MS is generally preferred over the CFA system. Initially developed in the early 2000s (Reinhardt et al., 2001; Müller et al., 2011; Della Lunga et al., 2014; Sneed et al., 2015), LA-ICP-MS has recently re-emerged with notable advancements in scan speed (1 mm $s^{-1}$ for single line profiles) and spatial resolution (35 μm in the ice matrix) (Bohleber et al., 2020). However, unlike CFA, LA-ICP-MS does not allow for simultaneous measurements of different proxies.

## Abbreviations

| | |
|---|---|
| CFA | Continuous Flow Analysis |
| ICP-MS | Inductively Coupled Plasma – Mass Spectrometry |
| ICP-QMS | ICP-Quadrupole Mass Spectrometer |
| ICP-SFMS | ICP-Sector Field Mass Spectrometer |
| ICP-TOFMS | ICP-Time-Of-Flight Mass Spectrometer |
| IRMS | Isotope-Ratio Mass Spectrometry |
| WS-CRDS | Wavelength Scanned – Cavity Ring-Down Spectrometry |
| OA-ICOS | Off-Axis Integrated Cavity Output Spectroscopy |
| OF-CEAS | Optical Feedback Cavity Enhanced Absorption Spectroscopy |
| GC-FID | Gas Chromatography – Flame Ionization Detector |
| IC | Ionic Chromatography |
| FIC | Fast Ion Chromatography |
| FLC-MS/MS | Fast Liquid Chromatography tandem mass spectrometry |
| Va | Vanillic acid |
| SyA | Syringic acid |
| LAS | Laser Absorption Spectrometers |
| RICE | Roosvelt Island Climate Evolution |
| EDML | Epica Dronning Maud Land |
| SARA | Spectroscopy by Amplified Resonant Absorption |
| CL | Chemiluminescence |
| SP2 | Single Particle Soot Photometer |
| rBC | Refractory black carbon |
| UBern-CFA | Bern-CFA |
| CIC-CFA | Copenhagen-CFA |

| | |
|---|---|
| IGE-CFA | Institute of Environmental Geosciences-CFA (Grenoble) |
| DRI-CFA | Desert Research Institute-CFA (Reno) |
| KOPRI-CFA | Korea Polar Research Institute-CFA (Incheon) |
| BAS-CFA | British Antarctic Survey-CFA (Cambridge) |
| ISP/UNIVE-CFA | Institute of Polar Sciences/Ca' Foscari University of Venice-CFA |
| LA-ICP-MS | Laser Ablation – Inductively Coupled Plasma – Mass Spectrometer |

**Data availability statement.** Data sharing is not applicable to this article as no new data were created or analyzed in this study.

**Acknowledgements.** The authors express their gratitude to all members of both the National Research Council – Institute of Polar Science of Venice (CNR-ISP) research group and the polar science group from the Department of Environmental Sciences, Computer Science, and Statistics, for their invaluable scientific support.

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