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ORIGINAL PAPER

Enhanced Ion Chromatographic Speciation of Water-Soluble $PM_{2.5}$ to Improve Aerosol Source Apportionment

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Abstract Ion chromatography (IC) is widely used to quantify sulfate, nitrate, ammonium, sodium, chloride, and potassium from $PM_{2.5}$ water extracts. IC hardware and software have progressed to allow a broader range of water-soluble compounds to be determined for the existing anion and cation programs and on the same solutions using analytical column, eluent, and detector modifications. Alkylamine, organic acid, and carbohydrate quantification by IC expands the number of source markers, especially for different types of biomass burning and secondary organic aerosols. Although modern systems are highly automated, internal quality control (QC) and external quality assurance (QA) programs are essential. QC includes detailed standard operating procedures, calibration over the range of expected concentrations, performance tests with independent standards, inspection of filters and chromatograms, and anion/cation balances. QA consists of independent system and performance audits, analysis of externally prepared performance samples, and interlaboratory comparisons. The additional water-soluble species provide compounds for speciated emission inventories, source markers to refine aerosol source apportionment, and increased understanding of global carbon, sulfur, and nitrogen cycles.

Keywords Ion · Ion exchange chromatography · Anions · Cations · Organic acids · Carbohydrates · Source markers · Receptor model · Source apportionment.

Introduction

Measurements of $PM_{2.5}$ (particulate matter with aerodynamic diameter less than 2.5 micrometers) elements, ions, and carbon fractions in chemical speciation networks are necessary, but not sufficient, for identifying and quantifying modern source contributions (Chow and Watson 2013; Watson and Chow 2013, 2015; Watson et al. 2016). Many elemental source markers are being eliminated from emission streams owing to their toxicity. As these primary PM emissions decrease, secondary organic aerosols (SOAs) are increasing in importance (Donahue 2013). Many of the SOA compounds absorb light at shorter (<600 nm) wavelengths, thereby affecting the Earth's radiation balance as Brown Carbon (BrC) (Laskin et al. 2015). The broad diversity of biomass fuels and burning conditions (Chakrabarty 2016), especially in countries outside of North America and Europe, require more specific markers to better determine control strategies. Peat burning, a common Asian combustion source (Wang et al. 2004), is poorly studied, even though it may have an important effect on the global carbon (Turetsky et al. 2015) and nitrogen (Galloway et al. 2004) cycles.

Watson et al. (2016) identify several proven analytical methods that can be applied to samples already acquired in PM speciation networks (Dabek-Zlotorzynska 2011; IMPROVE 2016; U.S.EPA 20016a; Zhang et al. 2012) as illustrated in Fig. 1. Watson et al. (2016) also associate the measured species with potential sources. This article elaborates on further analysis of the water-extracted compounds using ion chromatography (IC). IC with conductivity detection was developed in the mid-1970s (Small et al. 1975) to obtain multipollutant measurements with a single analysis for water-soluble ions. Analytes include fluoride (F^-), chloride (Cl^-), nitrite (NO_2^-), bromide

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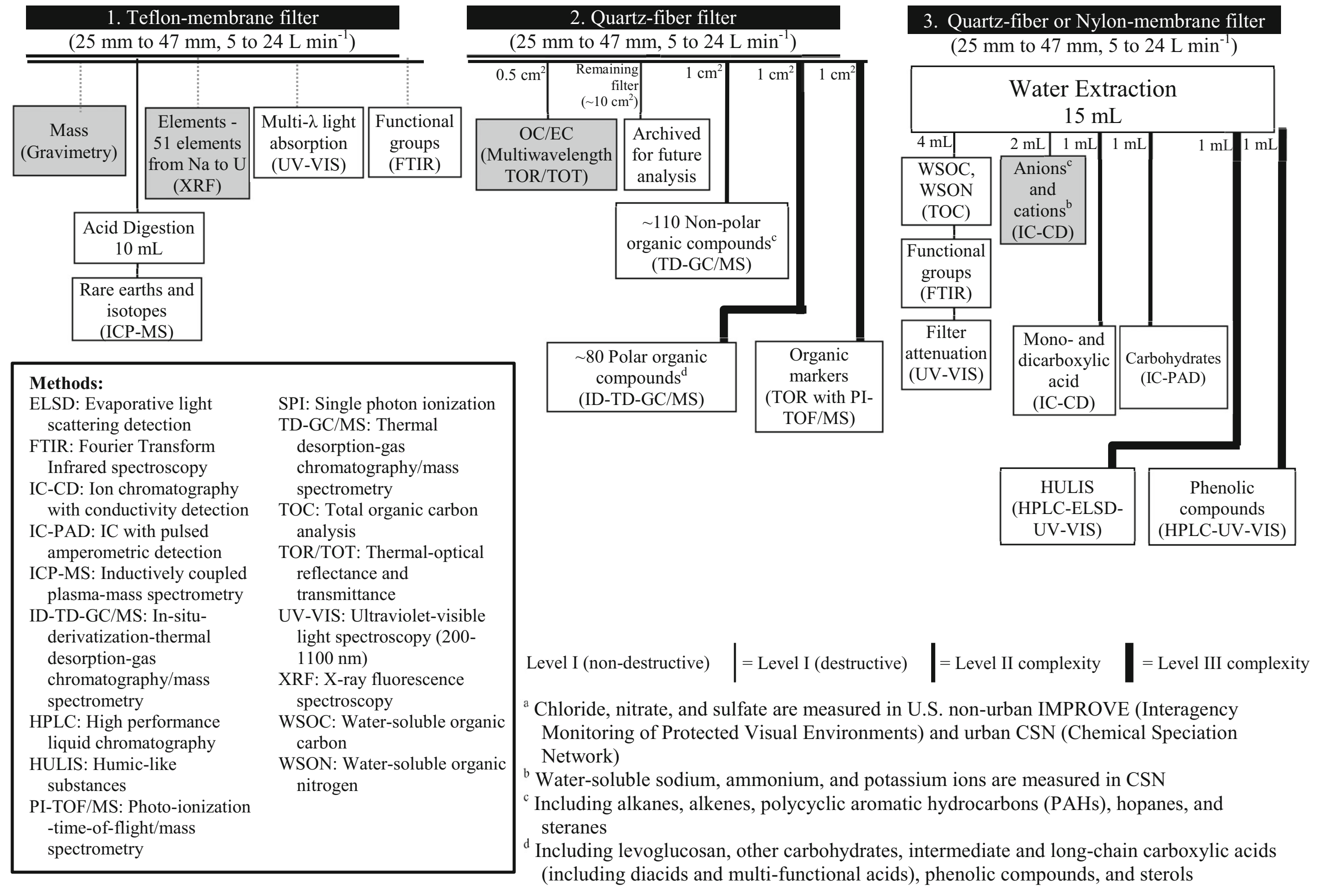

Methods:
ELSD: Evaporative light scattering detection
FTIR: Fourier Transform Infrared spectroscopy
IC-CD: Ion chromatography with conductivity detection
IC-PAD: IC with pulsed amperometric detection
ICP-MS: Inductively coupled plasma-mass spectrometry
ID-TD-GC/MS: In-situ-derivatization-thermal desorption-gas chromatography/mass spectrometry
HPLC: High performance liquid chromatography
HULIS: Humic-like substances
PI-TOF/MS: Photo-ionization-time-of-flight/mass spectrometry
SPI: Single photon ionization
TD-GC/MS: Thermal desorption-gas chromatography/mass spectrometry
TOC: Total organic carbon analysis
TOR/TOT: Thermal-optical reflectance and transmittance
UV-VIS: Ultraviolet-visible light spectroscopy (200-1100 nm)
XRF: X-ray fluorescence spectroscopy
WSOC: Water-soluble organic carbon
WSON: Water-soluble organic nitrogen

[a] Chloride, nitrate, and sulfate are measured in U.S. non-urban IMPROVE (Interagency Monitoring of Protected Visual Environments) and urban CSN (Chemical Speciation Network)

[b] Water-soluble sodium, ammonium, and potassium ions are measured in CSN

[c] Including alkanes, alkenes, polycyclic aromatic hydrocarbons (PAHs), hopanes, and steranes

[d] Including levoglucosan, other carbohydrates, intermediate and long-chain carboxylic acids (including diacids and multi-functional acids), phenolic compounds, and sterols

Fig. 1 Filter samples are commonly acquired in PM compliance and speciation networks (IMPROVE 2016; U.S.EPA 20016a). In these networks the Nylon-membrane filter is preceded by anodized aluminum denuder tubes (Chow 1993) that remove gaseous nitric acid so only PM nitrate is collected. *Shading* indicates the analyses and outputs that are currently obtained from these samples. Figure is adapted from Watson et al. 2016

(Br$^-$), iodide (I$^-$), nitrate (NO$_3^-$), sulfate (SO$_4^{2-}$), and phosphate (PO$_4^{3-}$) for anions; and sodium (Na$^+$), ammonium (NH$_4^+$), magnesium (Mg^{2+}), potassium (K$^+$), and calcium (Ca^{2+}) for cations. For PM$_{2.5}$ deposits on filters, samples are first extracted in distilled-deionized water (DDW). IC separates the water-extracted solutes with an ion exchange resin that delays their passage owing to different ion sizes and charges relative to the ionic eluent. This results in different retention times for individual ion quantification with a detector, typically a conductivity detector that measures the electrical current traversing the eluted solution. Prior to detection, the ion exchange column effluent enters a suppressor (membrane or column) where the eluent is neutralized, reducing its conductivity while retaining that of the ions of interest. Ionic compounds are identified by their elution/retention times and quantified by the conductivity peak area. Peak areas are related to concentrations from standard solutions for quantification. Although IC instruments can be set up to calculate concentrations by either peak area or peak height, laboratory tests show that peak area provides better accuracy and precision than those for peak height. Peak area is not affected by baseline shifts which commonly occur in IC analysis.

While most applications involve sampling onto filters with extraction and analysis in the laboratory, a growing number of in situ IC-based instruments are being used to obtain real-time concentrations with high time resolution (ten Brink et al. 2007; URG 2016; Weber et al. 2001). Sub-diurnal time resolution can also be obtained using the recently developed Sequential Spot Sampler (Hecobian et al. 2016) that impacts PM$_{2.5}$ into small wells on a carousel that can be subsequently extracted and analyzed with an automated laboratory IC.

Newer instrumentation and software have expanded the capability of IC to quantify selected organic compounds, several of which appear in the same spectra produced for inorganic ions and others that are detected using different columns, eluents, and detectors. This presentation updates a prior evaluation (Chow and Watson 1999) of IC methods applied to PM$_{2.5}$ filter samples that are acquired in compliance and speciation networks. It provides a brief summary of recent reviews on liquid chromatography (LC) applications to environmental samples, then defines the key terms used in IC analyses. This work summarizes tests on water-soluble extraction efficiencies for particles collected on different filter media and describes procedures for calibration, standardization, and quality control/quality assurance (QC/QA). It compares chromatograms from different systems, demonstrating the progress of improved hardware and software to better resolve water-soluble components. It proposes instrumental configurations that can obtain more information from the sample extracts than is currently achieved by simple inorganic anion and cation analyses.

Table 1 lists the analytes that can be obtained from the IC methods described here and associates them with potential pollution sources. The major ionic components of Cl^-, NO_3^-, SO_4^{-2}, Na^+, and NH_4^+ are essential for reconstructing PM mass (Chow et al. 2015) and estimating chemical light extinction to improve visibility (Cheng 2015; Pitchford et al. 2007; Watson 2002). Other ions, such as F^-, Br^-, I^-, PO_4^{3-}, Mg^{2+}, K^+, and Ca^{2+} which often go unreported, also have value as source markers. Water-soluble K^+ is a common biomass burning marker (Calloway et al. 1989), while water-soluble Ca^{2+} is found in transported Asian dust (Duvall et al. 2006). The addition of alkylamines, organic acids, and carbohydrates quantification by IC expands the number of source markers for biomass burning; fuel combustion; biodiesel, diesel, and gasoline engine exhaust; meat cooking; marine aerosol; and bioaerosol. Although several sources are potential contributors, these can be narrowed down by the study context and network design (Chow et al. 2002). Agricultural sources such as fertilizer and animal husbandry contributions would not be expected at urban sites, and biomass burning would favor SOA formation during cold winter periods.

Recent Reviews of Liquid Chromatography (LC) Methods

Liquid chromatography (LC) includes both IC and high performance liquid chromatography (HPLC) that have wide application to analyses of compounds dissolved in water. IC is used for most inorganic constituents, whereas HPLC speciates organic molecular constituents (Michalski 2016). HP uses a high-pressure pump [~3000 to ~6000 psi (pounds per square inch) or ~21,000 to ~41,000 kilopascals (kPa)] (Hartwell et al. 2013) to push the sample and eluent through the separating columns while lower pressures (<2,000 psi or ~14,000 kPa) are applied in IC. The types of stationary phase matrices, column packing methods, eluent compositions, and detection modes vary between IC and HPLC. IC variants, such as ion-exclusion chromatography (IEC), ion-pair chromatography (IPC), and reversed-phase liquid chromatography (RPLC), have also been used to separate hydrophilic molecules, biomolecules, and metal complexes (Fritz 1991; Gama et al. 2012; Gennaro and Angelino 1997; Michalski 2014; Nakatani et al. 2012). In tandem with mass spectrometric (MS) detection, as implemented in HPLC–MS, LC–MS, and LC–MS/MS, more complex water-soluble organic compositions, molecular structures, molar weights, and functional groups (Fenn 2002, 2003; Michalski 2014) can be quantified at ultra-low detection limits.

Recent reviews (Butt and Riaz 2009; Hartwell et al. 2013; Karu et al. 2012; Lucy and Wahab 2013; Michalski 2013, 2014; Nakatani et al. 2012; Olariu et al. 2015; Pohl 2013; Zhang et al. 2015) highlight the technological advances in IC systems and applications for environmental, pharmaceutical, clinical, and food chemistry samples. The sensitivity, selectivity, and linearity of IC systems can be modulated based on the selection of stationary phase properties and eluent compositions. Although IC methods began with conductivity detection (Small et al. 1975), other advanced detection techniques such as UV–VIS or diode array absorbance, amperometry, and potentiometry have been used to quantify additional water-soluble compounds (Buchberger 2001).

There are several suppliers of IC hardware (Lachat 2016; Metrohm 2016; Thermo-Dionex 2016; Waters 2016), with Thermo/Dionex being the major one. Figure 2 illustrates a generic IC set-up, but there are countless combinations of columns, eluents, and detectors that can be selected from the vendors' websites. The configurations described here are specified in Table 2. Basic components and terminology used in IC systems are documented in Table 3.

Filter Preparation, Receipt, Acceptance Testing, and Storage

Each batch of unexposed filters should be acceptance-tested with a visual inspection of every filter over a light table, with rejection of blank filters showing visual flaws, pinholes, or discoloration. One filter from each batch of 100 is extracted and analyzed for the intended species and the batch is rejected if excessive blank levels exceeding 0.5 μg per filter are detected. Nylon-membrane filter (Pall 2016) acceptance testing is especially important as it passively absorbs nitric acid vapors when exposed to the atmosphere (Bytnerowicz et al. 2005). Acceptance-tested filters are then placed in

Table 1 Pollution sources and detection limits for anions, cations, akylamines, organic acids, and carbohydrates[a]

Analyte (molecular formula)	Compound class	Nylon water extract (μg/mL)		Pollution source
		MDL[b]	LQL[b]	
Chlorine (Cl^{-})	Anion	0.002	0.014	Marine/sea salt; dry lakes; de-icing material; crustal material; biomass burning
Nitrite (NO_2^{-})		0.002	0.050	Fresh fossil fuel combustion
Nitrate (NO_3^{-})		0.004	0.070	Secondary ammonium nitrite or sodium nitrate; fertilizer
Sulfate (SO_4^{-2})		0.0008	0.017	Secondary ammonium sulfate, ammonium bisulfate, or sulfuric acid
Fluoride (F^{-})		0.002	0.006	Aluminum production
Bromine (Br^{-})		0.002	0.007	Marine aerosol; dry lakes; crustal material
Iodide (I^{-})		0.002	0.007	Marine/sea salt; dry lakes
Phosphate (PO_4^{-3})		0.0008	0.013	Fertilizer
Ammonium (NH_4^{+})	Cation	0.001	0.028	Secondary ammonium sulfate, ammonium bisulfate, or nitrate; agriculture/animal husbandry; fertilizer; wastewater treatment
Sodium (Na^{+})		0.007	0.037	Marine/sea salt; dry lakes; de-icing material;
Magnesium (Mg^{+2})		0.0016	0.002	Marine/sea salt; dry lakes
Potassium (K^{+})		0.0052	0.076	Biomass burning
Calcium (Ca^{+2})		0.0058	0.027	Marine/sea salt; transported Asian dust
Methylamine (CH_5N)	Akylamines	0.010	0.075	Derivatives of ammonia (NH_3); same sources as (NH_4^{+}) including agriculture/animal husbandry, and wastewater treatment
Dimethylamine (C_2H_7N)		0.010	0.054	NH_3 derivatives
Trimethylamine (C_3H_9N)		0.010	0.102	NH_3 derivatives
Formic acid/formate (CH_2O_2)	Organic acids	0.005	0.006	Biogenic POA[c]; biogenic SOA[d]; biomass burning
Acetic acid/acetate ($C_2H_4O_2$)		0.006	0.006	Biogenic POA; SOA
Lactic acid/lactate ($C_3H_6O_3$)		0.009	0.009	Marine aerosol[e]
Methanesulfonic acid (MSA)/methanesulfanate (CH_4SO_3)		0.011	0.011	Marine/sea salt; SOA[f]
Oxalic acid/oxalate ($C_2H_2O_4$)		0.010	0.010	Biomass burning; marine aerosol; SOA
Succinic acid/succinate ($C_4H_6O_4$)		0.035	0.035	Engine exhaust; meat cooking; biomass burning; SOA
Maleic acid/maleate ($C_4H_4O_4$)		0.020	0.025	Engine exhaust (photo-oxidation of benzene and aromatic VOCs from diesel and gasoline engines)
Malonic acid/malonate ($C_3H_4O_4$)		0.025	0.025	Engine exhaust; biomass burning; SOA
Glutaric acid/glutarate ($C_5H_8O_4$)		0.017	0.017	Engine exhaust; biomass burning; SOA
Levoglucosan ($C_6H_{10}O_5$)	Carbohydrates	0.001	0.020	Biomass burning
Mannosan ($C_6H_{10}O_5$)		0.001	0.040	Biomass burning
Galactosan ($C_6H_{10}O_5$)		0.002	0.040	Biomass burning
Glycerol ($C_3H_8O_3$)		0.002	0.003	Biodiesel engine exhaust; meat cooking
2-Methylerythritol ($C_5H_{12}O_4$)		0.003	0.009	Biogenic POA; SOA
Arabitol ($C_5H_{12}O_5$)		0.001	0.033	Bioaerosol—fungi
Mannitol ($C_6H_{14}O_6$)		0.002	0.109	Bioaerosol—fungi
Xylitol ($C_5H_{12}O_5$)		0.002	0.113	Biomass burning
Erythritol ($C_4H_{10}O_4$)		0.001	0.018	Biogenic POA[e]
Adonitol ($C_5H_{12}O_5$)		0.002	0.010	Bioaerosol—bacteria
Inositol ($C_6H_{12}O_6$)		0.004	0.010	Biogenic POA
Glucose ($C_6H_{12}O_6$)		0.002	0.113	Biogenic POA

Table 1 continued

Analyte (molecular formula)	Compound class	Nylon water extract (µg/mL)		Pollution source
		MDL[b]	LQL[b]	
Galactose ($C_6H_{12}O_6$)		0.001	0.056	Biogenic POA
Arabinose ($C_5H_{10}O_5$)		0.002	0.058	Biogenic POA
Fructose ($C_6H_{12}O_6$)		0.001	0.258	Biogenic POA
Sucrose ($C_{12}H_{22}O_{11}$)		0.009	0.110	Biogenic POA
Trehalose ($C_{12}H_{22}O_{11}$)		0.003	0.110	Bioaerosol—fungi

[a] See Watson et al. 2016 for a more complete list of source markers

[b] MDLs (minimum detection limits) and LQLs (lower quantifiable limits) are defined as three times the standard deviation of the instrument response to a known concentration of zero (i.e., a filter extract using laboratory blanks) and dynamic field blanks, respectively (Chow and Watson 1999). MDLs reflect instrument performance at low analyte concentrations, used to ensure no contamination of filter lots and establish instrument sensitivity. LQL provides background levels in passive field samples (the dynamic field blank may vary from each airborne particle sampling program and sampling location)

[c] *POA* primary organic aerosol

[d] *SOA* secondary organic aerosol

[e] Miyazaki et al. (2014)

[f] Methanesulfonic acid is produced by hydrolysis of dimethyl sulfoxide (Davison 1996), which is produced from the photochemical oxidation of dimethyl sulfide by marine algae and salt marsh plants (Baker et al. 1991)

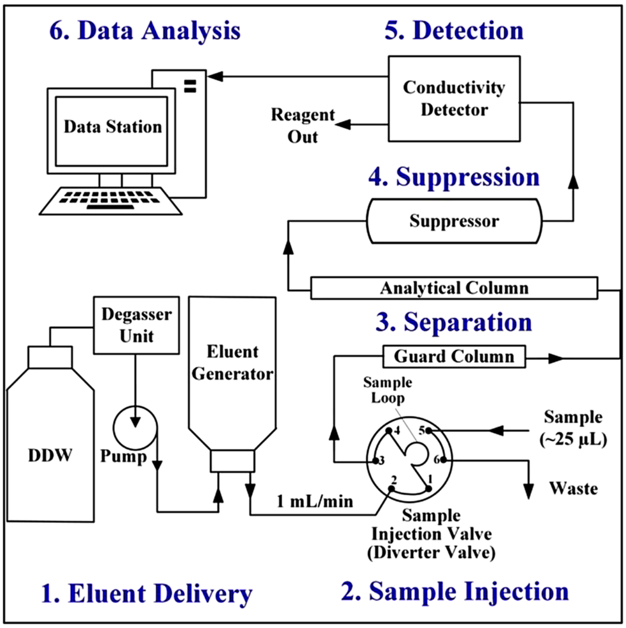

Fig. 2 Basic components of the ion chromatography system (based on the Thermo Scientific/Dionex ICS 5000$^+$configuration; *DDW* distilled-deionized water)

clean Petri slides or Petri dishes with bar-coded IDs, then sorted and sealed into ziplock bags prior to being loaded into sealed filter holders for shipment to and from field sites. This sealing intends to minimize passive absorption or deposition onto the filters. It is good practice to store filters and extracts at $<4\,^{\circ}$C in laboratory refrigerators with controlled access before ion analyses to minimize evaporation and contamination.

Filter Extraction

If available, the entire filter is immersed in 15 mL of DDW after placement in a polystyrene extraction tube that is labeled with the barcoded filter ID. If portions of the filter are to be used for other analyses, it can be sectioned into halves or quarters with one section used for extraction. Less than 15 ml of DDW can be used as the solvent, but it is important that the filter is completely immersed within the vial.

Extraction tubes (FisherScientific 2016) are capped, placed in extraction racks, and sonicated for 60 min in a temperature-controlled ($<25\,^{\circ}$C) sonication bath. Sonicator bath water is recirculated to minimize temperature increases from the dissipation of ultrasonic energy. After sonication, the extraction tubes are mechanically shaken [at a speed setting on 20 revolutions per minute (rpm)] for 60 min. Agitation assists the extraction of water-soluble particles embedded within the filter. The extracted filters are then aged for >12 h in a refrigerator at $<4\,^{\circ}$C. This process allows for complete dissolution of water-soluble components and the settling of any solid materials to the bottom of the vial (Stevens et al. 1978).

Although many tests of water extraction efficiency from filters have been conducted over the decades, few results from these tests have been published (Fosco and Schmeling 2007; Hoffer et al. 1979; Talebi and Abedi 2005). These tests involve either spiking the filter with known amounts of the ions using a microsyringe, comparing a less aggressive extraction with a more proven aggressive method, or by submitting an extracted filter to a second

Table 2 Examples of IC configurations for anion, cation, organic acid, and carbohydrate analyses

Analyte	Anions	Cations	Organic acids	Carbohydrates
IC instrument	Thermo Scientific /Dionex ICS-5000$^+$	Thermo Scientific/Dionex ICS-5000$^+$	Thermo Scientific /Dionex ICS-2100 or ICS-5000$^+$	Thermo Scientific/Dionex ICS-3000
Sample loop	25 µL	25 µL	30 µL	30 µL
Guard column	IonPac AG20 (4 × 50 mm)	IonPac CG16 (5 × 50 mm)	IonPac AG11 (4 × 50 mm)	CarboPac MA1 (4 × 50 mm)
Analytical column	IonPac AS20 (4 × 250 mm)	IonPac CS16 (5 × 250 mm)	IonPac AS11 (4 × 250 mm)	CarboPac MA1 (4 × 250 mm)
Micro-membrane suppressor	Anion electrolytically regenerated suppressor (AERS) 500	Cation electrolytically regenerated suppressor (CERS)-500	Anion self-regenerating suppressor (ASRS) 300 or AERS 500	AERS 500
Detector	ICS-5000$^+$ temperature controlled (30 °C) conductivity cell	ICS-5000$^+$ temperature controlled (30 °C) conductivity cell	Detection stability (DS6) heated conductivity cell (ICS-2100) or temperature controlled (30 °C) conductivity cell (ICS-5000$^+$)	Electrochemical detector optimized in pulsed amperometric mode, using gold (Au) as the working electrode and silver/silver chloride (Ag/AgCl) as the reference electrode
Eluent preparation	Eluent generator (EG)	Eluent generator	Eluent generator	Manual mixing
Eluent composition	Potassium hydroxide (KOH) gradient from 10 to 50 mM over ~17 min	Methanesulfonic acid (MSA) (40 mM)	Potassium hydroxide (KOH) (0.5–60 mM)	Sodium hydroxide (NaOH) (48–65 mM)
Flow rate	1.0 mL/min	1.0 mL/min	1.5 mL/min (ICS-2100) or 1.0 mL/min (ICS-5000$^+$)	0.4 mL/min
Pump	ICS-5000 dual pump (DP)	ICS-5000$^+$ dual pump	ICS-2100 single pump or ICS-5000$^+$ dual pump	ICS-3000 dual pump

Table 3 Descriptions of basic components commonly applied in ion chromatography

IC system component/terminology	Description
Distilled-deionized water (DDW)	Feeds nanopure system
Degasser unit	Removes dissolved gases and air bubbles from the eluent to ensure constant pressure and chromatographic resolution
Eluent	The liquid mobile phase that transports the sample solution through the ion exchange columns to the detector and facilitates separation by competing for ionic binding sites
Eluent generator	A pair of electrodes is separated by an ion exchange membrane. When a current is applied to the electrodes, water electrolysis generates hydronium or hydroxide ions (H_3O^+ or OH^-) at the anode or cathode, respectively, and counter-ions migrate from an eluent generation cartridge across a membrane to form the eluent. By controlling the current, accurate concentrations are generated (e.g., potassium hydroxide or methyl sulfonic acid)
Ion exchange resin or polymer	The medium (i.e., stationary phase) containing charged anionic or cationic exchange sites for ion exchange. It consists of high-molecular-weight insoluble functional groups that allow for the separation of ionic species from sample solutions based on ion charge and molecule size
Guard column (also termed as pre-column)	A small column placed upstream to prevent contamination or poisoning of the analytical column by removing particles and extraneous organic compounds
Analytical column (also termed as separation column, capillary column, or ion exchange column)	Separates the target ions in time before presentation to the detector. Contains the ion exchange resin and functional groups corresponding to the affinities of the target analytes and the mobile phase
Suppressor (also termed as microsuppressor, electrolytically regenerated suppressor, or self-regenerating suppressor)	Removes and replaces eluent counterions with regenerant ions (either H_3O^+ or OH^-). It converts the eluent to water or a weakly dissociated state prior to detection. The suppressor also lowers the background levels and maximizes signal-to-noise ratios
Suppressor regeneration	Converts and maintains an active form of suppression. Suppressor membranes are replenished by the sample stream after it leaves the conductivity detector and goes to waste. In combination with electrolytical regeneration, this allows for continuous operation for thousands of samples
Conductivity detector	Quantifies changes in electric current due to the presence of analyte ions and records the difference in voltage between electrodes
Pulsed amperometric detector (PAD)	Based on electrochemical detection using gold (Au) and silver/silver chloride (Ag/AgCl) as the working and reference electrodes, respectively
Ultraviolet–visible or diode array detector (UV–VIS or DAD)	Based on spectroscopic detection, it measures absorbance of single wavelengths (i.e., UV–VIS) or multiple wavelengths (i.e., DAD)
Gradient elution	Used to separate ions that may co-elute using lower eluent concentrations, and gradually shift to more concentrated eluent to reduce run time and separate ions that otherwise would take extended periods of time. Also used to elute multiple ions with widely different retention times, thus reducing total run time. The concentration or composition of the eluent can be altered in a single run to facilitate the ion separation and to increase the resolution of the target analytes (due to high background conductance, sodium carbonate/bicarbonate eluents are not appropriate for gradient elution)
Isocratic elution	Employs a fixed concentration level and preset flow rate. This mode maintains a constant baseline during analysis. This is the most common mode applied to $PM_{2.5}$ filter extracts
Retention time	The time from sample injection to the time the detector signal reaches its maximum value. This delay is used to associate the desired analytes with the detector responses
Resolution	A measure of column efficiency and capacity by quantitatively differentiating two eluted peaks. Narrower peak widths imply higher resolution
Distilled-deionized water (DDW) dip	A negative peak occurs on the chromatogram (usually with the sodium carbonate/bicarbonate eluent) upon injection of analyte, corresponding to the DDW in the sample extract. As the conductance of DDW is often less than that of the suppressed eluent, ions eluting near the DDW dip are co-eluted or suppressed (e.g., fluoride and chloride)

extraction (Mouli et al. 2003). Derrick and Moyers 1981 examined extraction methods for Teflon-membrane and quartz-fiber filters. Teflon is hydrophobic, and DDW does not wet the surface or penetrate within the membrane (Wolfson 1980). Pure DDW, sodium carbonate/bicarbonate eluent, and perchloric acid by themselves yielded <80% efficiencies after 15 min of sonication and <2 h of aging for nitrate, sulfate, and ammonium. However, the DDW extraction yielded >95% efficiencies for these ions when analyzed after 24 h of aging following sonication. Chow and Watson (1999) noted the hydrophobic nature of Teflon-membrane filters that require applications of a wetting solution (e.g., 200 µL ethanol or methanol) onto the filter deposit surface to ensure complete dissolution of the analyte ions.

Nylon-membrane filters are hydrophilic, as evidenced by their soaking up of a water droplet, in contrast to the Teflon-membrane on which the droplet remains on the surface. Yu et al. (2005) found equivalent nitrate and sulfate concentrations on Nylon-membrane filters extracted in DDW and IC eluent, both with 30–45 min of sonication. They did not report the aging time prior to analysis, but it is evident that the eluent extraction is unnecessary. This is a useful result, as the sodium carbonate/bicarbonate IC eluent for anions would interfere with possible cation analysis on the extracts. A pure DDW extraction is preferable

Extraction efficiencies determined from two sets of 20 Nylon-membrane filters spiked with known concentrations of mixed anion standards are compared in Fig. 3. Recovery rates range from 100–103.9% and 92–96% for Laboratories A and B, with averages and standard deviations of 100.2 ± 0.8% and 94 ± 2.1%, respectively.

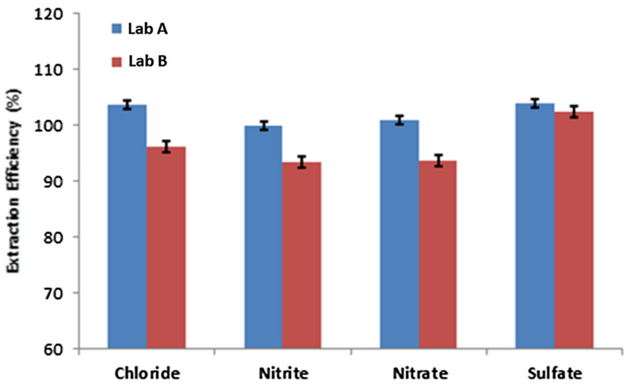

Fig. 3 Extraction efficiencies of two sets of standard spiked (2 µg/mL mixed anion standards) Nylon-membrane filters following two laboratory procedures (Lab A uses 15 mL extraction volume, followed by 60 min each of sonication and mechanical shaking with ∼12 h of refrigeration aging; Lab B uses 20 mL extraction volume, followed by 30 min of sonication, then *left* at room temperature for 24 h before refrigeration overnight)

IC for Anions, Cations, Organic Acids, and Carbohydrates

Thermo/Dionex ICs are most commonly used, although alternatives are also available. The older models (e.g., DX-500, DX-600, and ICS-2000) have been used in the past (Chow et al. 1990; Watson 1991) and are adequate for inorganic anion and cation analyses. These instruments are still available on the used-instrument market, along with replacement parts and supplies. They have been largely superseded by later model hardware and software.

Anions

Anion columns use carbonate or hydroxide-selective anion exchange resins that can accommodate a reasonable (∼2000) sample throughput. An anion electrolytically regenerated suppresser (AERS) is used to reduce background conductivity by exchanging the K$^+$ with hydrogen ion (H$^+$) to produce water in the case of hydroxide (or similarly convert carbonate to bicarbonate and/or carbonic acid). An eluent generator is used to produce a 15 millimole (mM) potassium hydroxide solution for isocratic elution followed by conductivity detection.

Anion chromatograms from two systems are compared in Fig. 4. The ICS-5000$^+$ configuration (Fig. 4b) has higher sensitivity with improved chromatographic resolution. This is partially due to the carbonate/bicarbonate buffer system used by the ICS-3000, which does not completely eliminate background conductivity. This is most evident for the fluoride or chloride peak, which often interferes with the DDW dip. As the conductance of DDW is often less than that of the suppressed eluent, fluoride or chloride eluting near the DDW dip is co-eluted or suppressed. Background subtraction and manual adjustments are required for the older IC systems to quantify potential co-eluted species and peak overlaps. This is labor-intensive and results in large uncertainties in ion concentrations (Chow and Watson 1999). Nitrite was also found in this sample, though it was below ICS-3000 minimum detection limits (MDLs) (Fig. 4a).

The carbonate peaks in Fig. 4b are dominated by artifacts rather than components of the aerosol deposit. Despite de-gassing of the water by helium sparging, this interference results from carbon dioxide (CO$_2$) dissolved in the DDW or eluent. The carbonate peak is separable from the other anions and causes no bias to their quantification. It may be reduced by purging the sample chamber with an inert gas and minimizing the time between extraction and analysis.

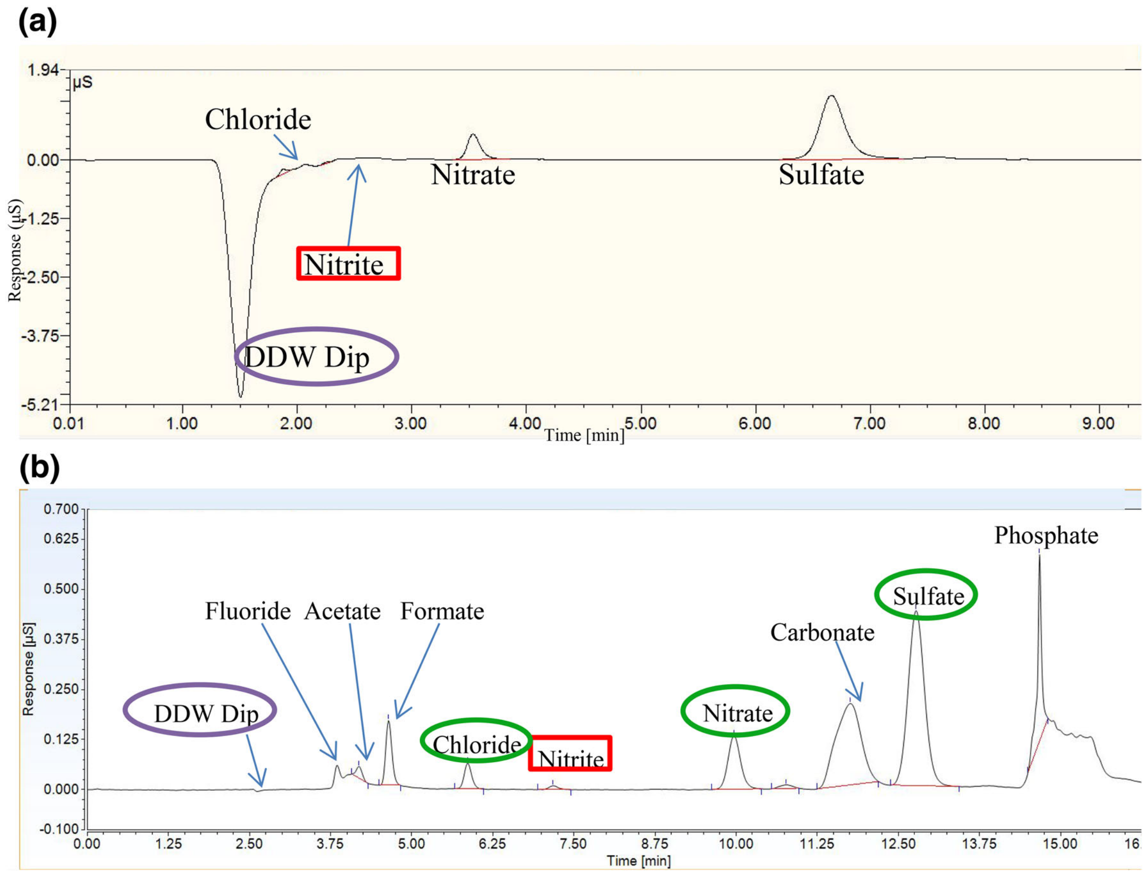

Fig. 4 Anion chromatograms for: **a** ICS-3000 with sodium carbonate/bicarbonate eluent; and **b** ICS-5000$^+$ with potassium hydroxide eluent for a sample from October 15, 2014, collected at Clinton, TX, USA (*DDW* distilled-deionized water). The ICS-5000$^+$ chromatogram minimizes the DDW dip, has a more constant baseline, and better detects nitrite for this sample. It also resolves additional compounds. *Y* axis is the response in microsiemens (µS)

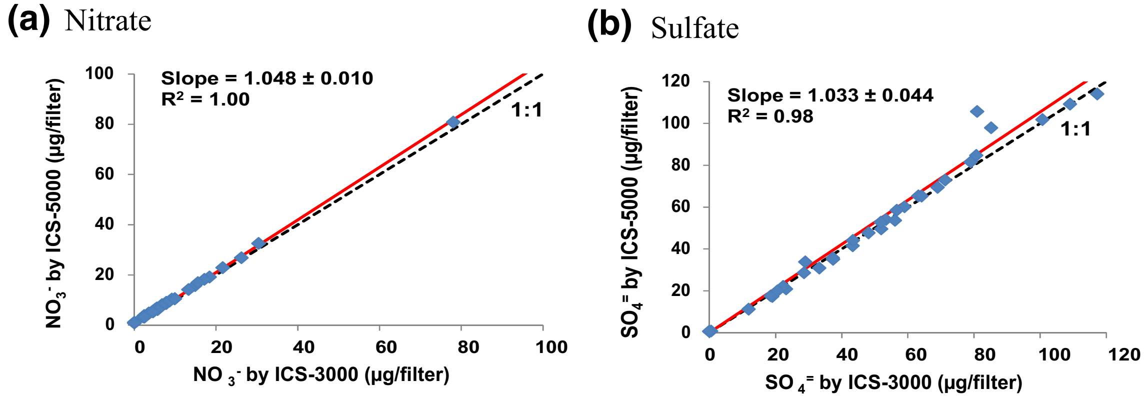

Fig. 5 Comparison between Dionex ICS-5000$^+$ and ICS-3000 systems for: **a** nitrate; and **b** sulfate with 34 Texas $PM_{2.5}$ samples (eluent composition is 15 mM potassium hydroxide in ICS-5000$^+$and is 35 mM sodium carbonate/10 mM sodium bicarbonate in ICS-3000)

Figure 5 compares nitrate and sulfate concentrations for the same sample extracts analyzed by the ICS-5000$^+$ and the ICS-3000 systems. There is good agreement ($0.98 \le R^2 \le 1$) for the replicate analyses, indicating that the eluent difference does not affect the results for these important components.

Cations

Cation columns (i.e., either the guard column or analytical column) use a hydrophilic and carboxylate functionalized cation exchange resin that can accommodate a reasonable

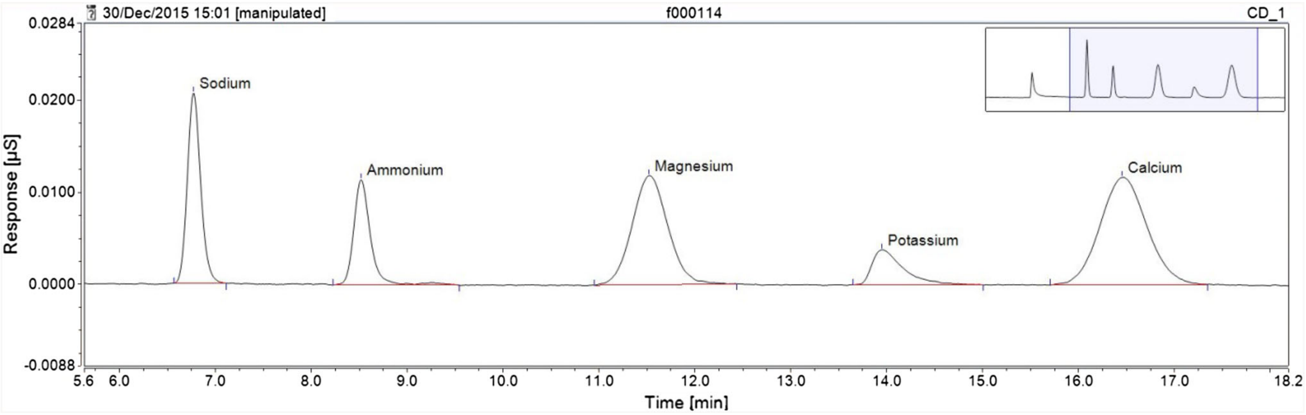

Fig. 6 Chromatogram for cation analysis of ambient filter sample collected in November 20, 2015, at Reno, NV, USA. *Y* axis is the response in microsiemens (µS)

($\sim$2500) sample throughput. A cation electrolytically regenerated suppressor (CERS) is used to reduce background conductivity by exchanging the buffer anion (e.g., methane sulfonate or sulfate) with hydroxide ion (OH^-), and an eluent generator is used to produce 40 mM methanesulfonic acid (MSA) solution for isocratic elution followed by conductivity detection. Figure 6 shows an example of the cation chromatogram with $\sim$20-min analysis time per sample.

Both gaseous ammonia (NH_3) and particle ammonium are important atmospheric constituents that contribute to the global nitrogen cycle (Fowler 2015), elevated $PM_{2.5}$ (Wang et al. 2013), and ecosystem deposition (Granath et al. 2014). If ammonium is the major cation of interest, a fast run cation column (e.g., 4 × 250 mm CS12A) can be used with a 33 mM MSA eluent composition for a 3-min analysis time. Although there are potential savings on analysis time (i.e., from 20 to 3 min per run), these are not necessarily achieved when other cations are present, as additional rinsing time is needed to elute the remaining cations (e.g., water-soluble magnesium, potassium, and calcium); sample carry-over may cause cross-contamination. The $\sim$20-min analysis time ensures clean separation. The only cost savings would be the time reduction in system calibration and chromatogram validation, as fewer ion species are needed to prepare calibration standards and only a single peak is subject to verification.

The conductivity/concentration relationship is non-linear for ammonium at high concentrations and a quadratic curve is needed to fit the calibration standards. Figure 7a shows an upper limit of 10 µg/mL standard may underestimate the ammonium concentration. The linear curve is improved with a calibration curve from 0.005 to 2 µg/mL (Fig. 7b), with best linearity found with an upper limit of 1 µg/mL (Fig. 7c). For cation analyses, the upper limit can be set at 10 µg/mL for water-soluble sodium, magnesium, potassium, and calcium ions and at 1 µg/mL for ammonium. Values above these require dilution and re-analysis.

Alkylamines

Alkylamines, derivatives of ammonia, can serve as markers for agricultural sources (Ge et al. 2011) and are determined following the cation procedure. Dimethylamine may co-elute with the magnesium ion and trimethylamine may co-elute with the calcium ion; however, their concentrations are usually small compared to the inorganic ions. Using gradient eluent mode, Fig. 8 shows that the three alkylamines can be quantified along with ammonium and four other inorganic cations within a single $\sim$30-min run.

Organic Acids

Organic acids derive from a mixture of anthropogenic sources, including biomass burning; biodiesel, diesel, and gasoline engine exhaust; marine aerosols; meat cooking; biogenic; as well as primary organic aerosols (POAs) and SOAs (Hawkins et al. 2010; Kundu et al. 2010; Millet 2015). Figure 9 shows the extension of anion analysis with nine organic acids in a single run. The organic acids most commonly found in ambient samples includes four mono-carboxylic acids (i.e., lactate, acetate, formate, and MSA) and five di-carboxylic acids (i.e., glutarate, succinate, malonate, maleate, and oxalate) (Brent et al. 2014; Karthikeyan et al. 2007) that can be speciated along with commonly measured anions as specified in Table 2.

Some of these organic acids could possibly interfere with inorganic anion peaks if present in sufficient quantities. With proper gradient elution, Fig. 9 shows that early eluting mono-carboxylic acids (e.g., acetate, formate, or MSA) do not interfere with the chloride peak and

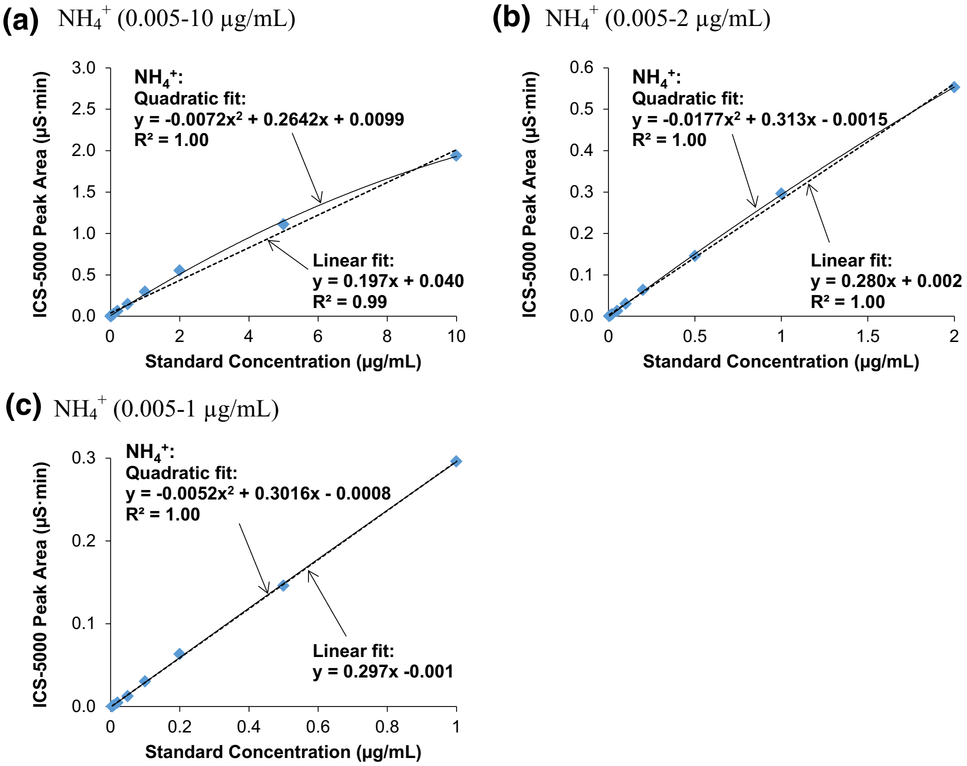

Fig. 7 Example of ammonium (NH_4^+) calibration curves of a Thermo Scientific/Dionex ICS-5000$^+$ with upper limits of: **a** 10 µg/mL, **b** 2 µg/mL, and **c** 1 µg/mL. The linear response is found with 0.05–1 µg/mL range

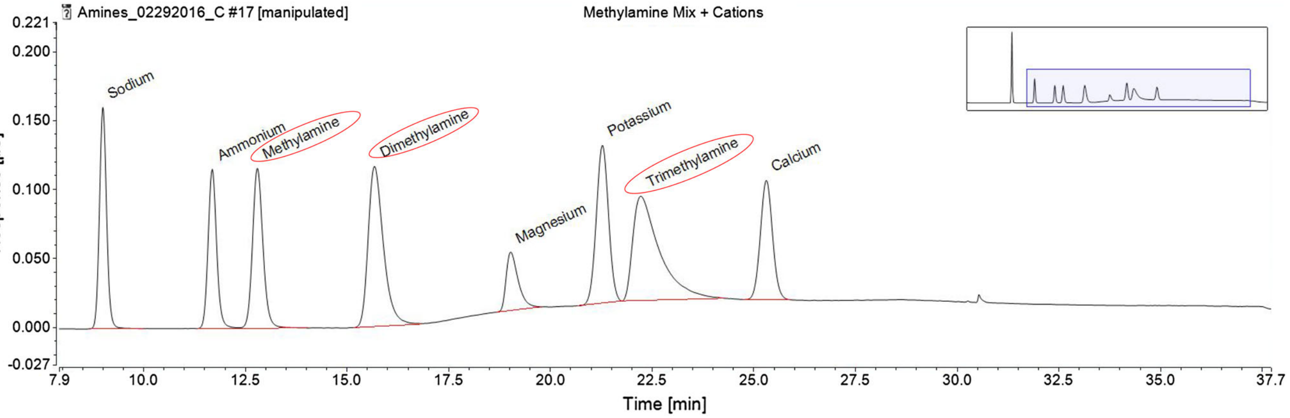

Fig. 8 Example chromatogram for the separation of the three alkylamines (i.e., methylamine, dimethylamine, and trimethylamine) from ammonium and other cations (i.e., water-soluble sodium, magnesium, potassium, and calcium ions). Based on a standard solution of 0.1 µg/mL using a Thermo Scientific/Dionex ICS-5000$^+$ system. The di- and trimethylamine are separated using gradient elution mode starting with a 25 mM concentration for 12 min, increasing to 55 mM concentration for 13 min and followed by a 25 mM concentration for 5 min. This allows the three alkylamines to be quantified along with ammonium and four other inorganic cations within a single ~30 min run. *Y* axis is the response in microsiemens (µS)

dicarboxylic acids (e.g., maleate or oxalate) do not interfere with the sulfate peak.

Carbohydrates

Carbohydrates are markers for biomass burning, bioaerosols, biogenic POAs, and SOAs. The commonly used biomass burning marker, levoglucosan, as well as its isomers mannosan and galactosan, can be quantified by IC using a pulsed amperometric detection (PAD) (Engling 2006; Garcia et al. 2005; Iinuma et al. 2009; Zhang 2013), with applications in several field studies (Caseiro et al. 2007; Ho 2015; Iinuma et al. 2009; Sullivan et al. 2011; VandenBoer et al. 2012; Yttri 2015; Zhang 2013). IC-PAD integrates HPLC and IC techniques by combining anion exchange with electrochemical detection. It is based on the

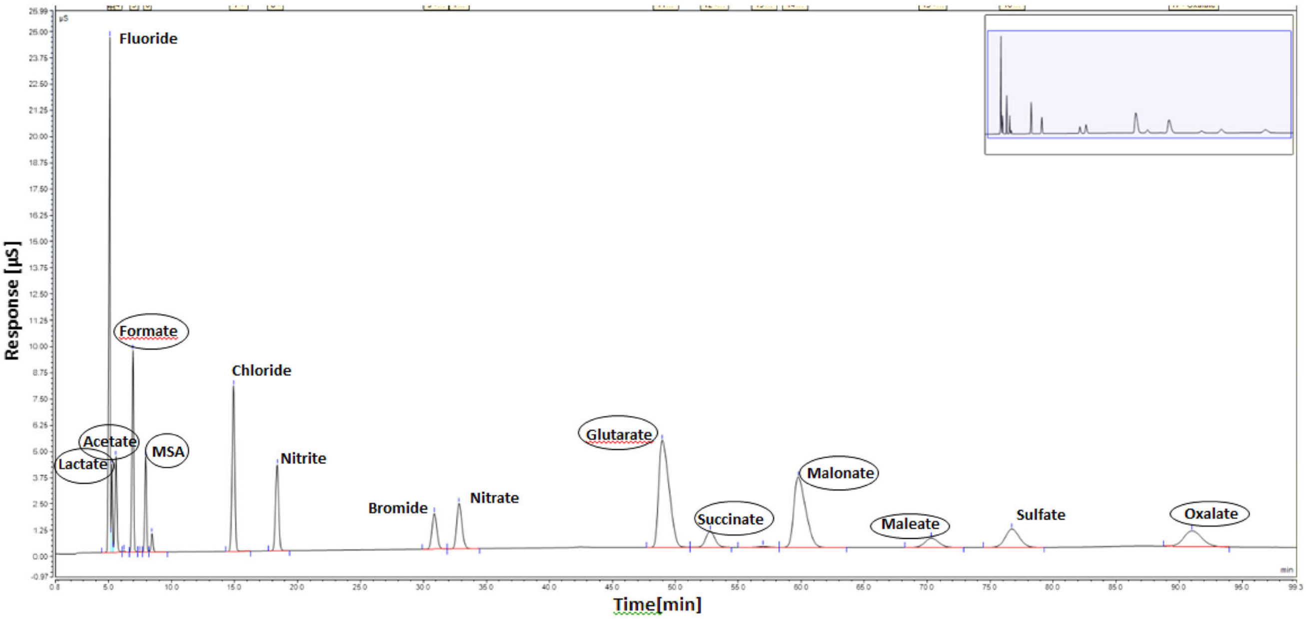

Fig. 9 Example of chromatogram showing the presence of seven anions (i.e., fluoride, bromate, chloride, nitrite, bromide, nitrate, and sulfate) and nine organic acids including four monocarboxylic acids (i.e., acetate, lactate, formate, and methane sulfuric acid [MSA]) and five dicarboxylic acids (i.e., glutarate, succinate, malonate, maleate, and oxalate). *Y* axis is the response in microsiemens (µS)

principle that multiple hydroxyl (OH) groups are detected by amperometry, using specific voltages to induce oxidation of individual species and to elute from the anion exchange column. Carbohydrate species are separated upon ionization with a strong alkaline eluent (see Table 2).

IC-PAD is cost-effective as it allows for detection of polar organic compounds using portions of the same DDW sample extract available for anion or cation analyses without the need for chemical derivatization, solvent extraction, and/or extract volume reduction (as is required for gas chromatography–mass spectrometry (GC–MS) analysis of polar organic compounds). Other analytical methods used for polar organic compounds require a separate sample for solvent extraction followed by GC–MS (Mazurek et al. 1989). An additional advantage of the IC-PAD method is its sensitivity and selectivity for multiple poly-hydroxy compounds (i.e., anhydrosugars and sugar alcohols). The electrochemical detector is optimized in pulsed amperometric mode, allowing selective measurement of the anhydrosugars, along with other carbohydrates and sugar alcohols. Figure 10 shows the chromatogram of markers for biomass burning (e.g., levoglucosan, mannosan, and galactosan); fungi (e.g., arabitol, mannitol, and trehalose); bacteria (e.g., adonitol); and biogenic POAs (e.g., erythritol, inositol, glucose, galactose, arabinose,

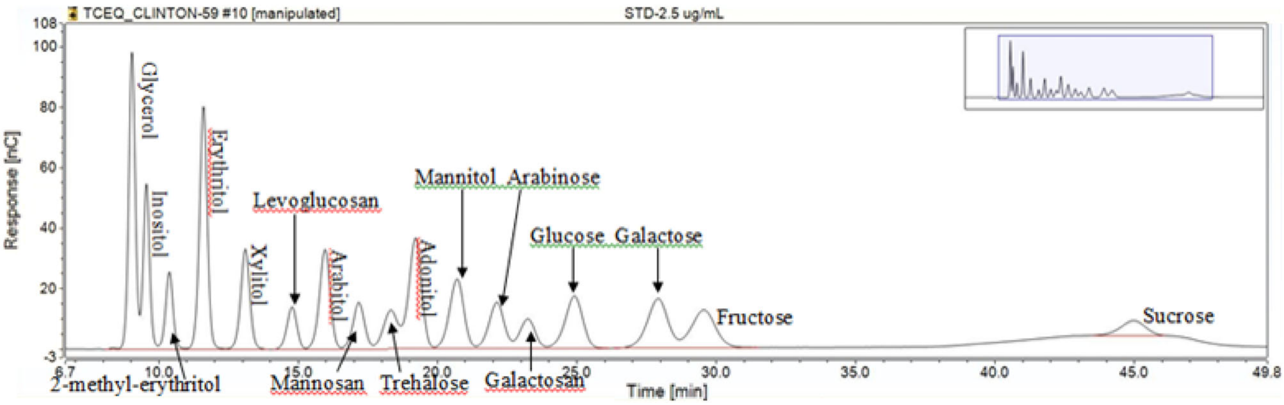

Fig. 10 Chromatogram from analysis of a standard solution (at 2.5 µg/mL level) for 17 carbohydrates (i.e., glycerol, inositol, 2-methyl-erythritol, erythritol, xylitol, levoglucosan, arabitol, mannosan, trehalose, adonitol, mannitol, arabinose, galactosan, glucose, galactose, fructose, and sucrose). *Y* axis is the response in nanocoulombs (nC)

Table 4 Quality control (QC) activities for ion chromatography analyses

QC activity	Purpose	Frequency	Standard	Acceptance criteria	Response/action
Multipoint calibrations (at 10 concentration levels from 0.005 to 10 μg/mL)	Establish instrument response curves to known concentrations	Every batch of ~120 samples	NIST[b] - Certified standards	±5%	Recalibrate
Minimum detection limit (MDL)	Ensure no contamination of filter lots and establish instrument sensitivity	Initially, then quarterly or after major instrument change	Lab blanks	Within ±10% of previous limits	Troubleshoot instrument and check filter lots
Lower quantifiable limit (LQL)	Provide background levels in passive field samples	Quarterly	Field blanks	Within ±10% of previous limits	Troubleshoot instrument and check filters
Distilled-deionized water (DDW)	Establish chromatogram background of filter batch and clean column	Thrice every batch of ~120 samples	DDW	Within three standard deviations of MDLs	Verify instrument response to DDW without extraction
Method blank [c]	Verify chromatogram baseline after sample extraction	Thrice every batch of ~120 samples	DDW	Within three standard deviations of MDLs	Check instrument response for DDW with extraction
QC standards (NIST-certified standard from Thermo Scientific)	Ensure instrument accuracy with independent standards	Every 20th sample	Multi-component solution	±10%	Samples before QC standard and previous standards reanalyzed
QC performance (NIST-certified) standard from ERA WasteWatR™	Ensure instrument accuracy with independent standards	Every 20th sample	Multi-component solution	±10%	Samples before QC standard and previous standards reanalyzed
Replicates	Ensure sample precision among the IC systems and between different analysis dates	10% of samples	NA	±10% when value >10 × MDL	Reanalysis of previous samples
Level 1 Data Validation	Inspect chromatograms for abnormalities or potential interferences	Every sample	NA	Per SOP[d]	Sample reanalysis or flagging per SOP

[a] *NA* not applicable

[b] *NIST* National Institute of Standards and Technology (Gaithersburg, Maryland, USA)

[c] *Method Blank* 15 mL DDW solution that follows the same extraction procedure as that for samples

[d] *SOP* standard operating procedure

Table 5 Quality assurance (QA) activities for ion chromatography analyses

QA activity	Purpose	Frequency	Auditor[a]	Acceptance criteria	Response action
Internal system and performance audits	Ensure compliance with operational and quality system procedures	Every year	Performed by internal QA manager	Conformance with lab SOPs[b], QAPPs[c], quality manual, and 2009 TNI[d] standard	Prepare preventive or corrective actions based on audit findings and follow up to ensure completion of specified actions
Technical system audits	Assess adequacy of and conformance with good laboratory practices and QA/QC procedures	Every 3 years	Performed by external auditor	Conformance with good laboratory practices and adherence to lab SOPs	Prepare and implement preventive and corrective actions as needed based on audit findings
Quality system audit	Assess adequacy of and conformance with quality system	Every 3 years	Performed by external auditor	Conformance with good laboratory practices and adherence to lab SOPs	Prepare and implement preventive and corrective actions as needed based on audit findings
Performance evaluations and laboratory inter-comparisons	Assess comparability of analytical results with standards and other laboratories	Every year	Performed by external audit team	Within specified limits and agreement with other labs using different criteria for IC ions[e]	Prepare and implement preventive and corrective actions as needed based on findings

[a] For US speciation networks, external auditors include the US Environmental Protection Agency (U.S.EPA 2016b) and the National Environmental Laboratory Accreditation Program (NELAP) (TNI 2016)

[b] *SOP* standard operating procedure

[c] QAPP Quality Assurance Project Plan

[d] *TNI* NELAC (National Environmental Laboratory Accreditation Conference) Institute

[e] Includes NO_3^-, SO_4^{2-}, Na^+, NH_4^+, and K^+

fructose, and sucrose). Biogenic SOA markers (e.g., 2-methyl-erythritol) derived from oxidation of isoprene can also be identified and quantified with a single ~60-min run.

IC Analysis Procedures, Quality Control (QC), and Quality Assurance (QA)

Several standard operating procedures (SOPs) are available that can serve as starting points for establishing an IC laboratory (Pfaff 1997; U.S.EPA 2000, 2007). SOPs codify the actions that are taken to implement a measurement process over a specified time period (Watson et al. 2001). The latest scientific information should be incorporated into SOPs with each revision. QC and QA activities are important parts of each SOP, as specified in Tables 4 and 5, respectively.

System calibration relates the sensor output to known concentrations as determined by standard solutions that span the range of expected concentrations. Although these standards can be prepared by carefully weighing and dissolving dehydrated salts in known amounts of DDW, it is now possible to purchase certified solutions (AlfaAesar 2016; ERA 2016) that can be diluted to the appropriate concentrations. The stock solution of 100 µg per milliliter (mL) is diluted to 10 levels of working standards ranging from 0.005 to 10 µg per mL. It is good practice to use solutions from one supplier for calibration and from another supplier for QC performance tests to assure that the concentrations are accurate. Table 1 includes MDLs and lower quantifiable limits (LQLs) achievable with the Table 2 configurations. MDLs are typically much lower than the LQLs derived from field blanks, which include passive deposition and adsorption of gases.

After analysis, each chromatogram is examined for: (1) proper operational settings and peak identification; (2) correct peak shapes and integration windows; (3) peak overlaps; (4) correct background subtraction (if needed); and (5) QC standard comparisons. Level I data validation (Watson et al. 2001) involves chromatogram inspection for each analysis, applying range checks to batches of data and investigating outliers, ensuring differences in replicate analysis comparable to those of differences in long-term averages, and examining consistency between calibration standards and performance tests with independent QC standards. Analysts need to re-calculate ion concentrations from existing chromatograms when there is evidence that peaks were not adequately defined by the peak-processing software, and re-analyze batches of samples that do not pass validation tests. Level I data validation flags are assigned that indicate filter appearance, filter damage, unusual deposits, excessive filter loading, and other anomalies observed during the analysis. Cation/anion balances (Chow et al. 1994) are also a useful validation tool when both are measured, although these may not balance when unquantified hydrogen ions are present, as for sulfuric acid.

Concentrations for each species are reported for each filter after normalizing to the extraction volume. Analysis precisions are calculated for different concentration intervals as:

$$\mathrm{CV} = \frac{\sum_{i=1}^{N} \frac{2\times\left|c_i - c_{i,r}\right|}{c_i + c_{i,r}}}{N} \tag{1}$$

$$\sigma_{\mathrm{cion}} = \sqrt{\left(\mathrm{CV}\times c_i\right)^2 + \left(\mathrm{MDL}/3\right)^2}, \tag{2}$$

where *CV* is the coefficient of variation for each ion; N is the number of samples, c_i is the concentration of initial analysis of sample $i$for each ion, $c_{i,r}$ is the concentration of sample "i" replicate analysis for each ion; *MDL* is defined as three standard deviations of laboratory blanks for each ion; σ_{cion} is the precision of c_{ion}.

Data are transmitted to a master data base in any specified format, which usually includes a separate record for each sample with the sample ID, filter lot number, analysis date, validation flags, filter loading values, and precision for each element. These are associated with field data, such as air sample volume, through the sample ID for a final output in µg/m^3.

QA consists of external examinations of the measurement process, as delineated in Table 5. These include laboratory certifications (TNI 2016), inspections and systems audits (Taylor 2005, 2007), and performance audits/interlaboratory comparisons (Smiley 2005, 2007, 2009, 2010; Taylor 2008). These are often required by an external sponsor, but they are good practice even if not required.

Summary and Conclusions

IC has progressed from simple analyses of inorganic anions and cations to a versatile laboratory tool applicable to a large range of water-soluble inorganic and organic compounds. Modern hardware and software allows several organic compounds to be discerned along with the normal anion and cation analyses. Modifications of columns, eluent compositions, concentrations, and detectors allow further characterization of alkylamines, organic acids, and carbohydrates that are markers for biomass burning, fuel combustion, engine exhaust, meat cooking, marine aerosol, and bioaerosol (e.g., fungi and bacteria) as well as primary and secondary organic aerosols. Labor is reduced by autosampling and sample routing, such that a single sample tray could be used for multiple analyses described here.

These additional water-soluble species are useful to better understand their abundances and variations in source profiling and to refine aerosol source apportionment.

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Compliance with ethical standards

Conflicts of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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