Journal of Chromatography A, 1266 (2012) 17–23

Contents lists available at SciVerse ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

A comprehensive and suitable method for determining major ions from atmospheric particulate matter matrices

José S.S. Domingos[a], Ana Carla D. Regis[a], João V.S. Santos[b], Jailson B. de Andrade[a,c,d], Gisele O. da Rocha[a,c,d,*]

[a] Universidade Federal da Bahia, Instituto de Química, 40170-290, Campus de Ondina, Salvador, BA, Brazil
[b] Instituto Federal de Educação, Ciência e Tecnologia Baiano, 45995-000, CP 66 Campus-Teixeira de Freitas, BA, Brazil
[c] Centro Interdisciplinar de Energia e Ambiente – CIEnAm, Universidade Federal da Bahia, Canela, 40170-290 Salvador, BA, Brazil
[d] INCT de Energia e Ambiente, UFBA, 40170-290 Salvador, BA, Brazil

ARTICLE INFO

Article history:
Received 11 June 2012
Received in revised form 10 August 2012
Accepted 22 August 2012
Available online 3 October 2012

Keywords:
Major ions
Water soluble species
Water soluble organic compounds
Ion chromatography
Atmospheric particulate matter
Environmental samples

ABSTRACT

The present study proposes an analytical methodology that employs ion chromatography–conductivity detection for simultaneous quantification of inorganic (F^-, Cl^-, NO_3^-, SO_4^{2-}, and PO_3^-), monocarboxylate ($HCOO^-$, CH_3COO^-, propionate, n-butyrate, lactate, and pyruvate), dicarboxylate (oxalate and succinate), and tricarboxylate anions (citrate), as well as crustal cations (Li^+, Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}) at low pg m^{-3} range in airborne particle samples in one single run. The optimized conditions for anions were as follows: 0.6 mmol L^{-1} KOH for 0–14 min, 0.6–15 mmol L^{-1} KOH 14–20 min, 15–38 mmol L^{-1} KOH during 20–32 min and finally returned to 0.6 mmol L^{-1} for a period of 3 min, thereafter the eluent flow rate was 0.38 mL min^{-1}. Similarly, for cations, isocratic elution was adjusted to 0.36 mL min^{-1} at 17.5 mmol L^{-1} H_2SO_4. LOD ranged 3.0–130 pg m^{-3} and LOQ was within 10–400 pg m^{-3} (Li^+ and PO_4^{3-}, respectively) as well as recoveries ranged 89% (Ca^{2+}) to 120% (Li^+). Major ions were successfully determined in real PM1 and PM2.5 samples. The method used here was found to be a comprehensive, simple, cheap and reliable procedure for studying ions in particulate matter (PM) samples even those from remote areas or near ecosystem natural conditions.

1. Introduction

Chemical characterization of atmospheric particulate matter is important for assessment of climate change on global level, on human health issues, and on issues regarding materials and ecosystems. Furthermore, such a characterization is necessary to gain a better comprehension of atmospheric chemical processes and to develop more consistent atmospheric models. Many chemical constituents of particulate matter (PM) are commonly used as source tracers and/or particulate matter precursors such as acidic and basic vapors and their respective ions. They may also be good representatives of secondary atmospheric pollutants mainly associated with crustal cations (Na^+, K^+, NH_4^+, Mg^{2+} and Ca^{2+}) [1–6].

Water-soluble species (WSS) (for instance crustal cations, inorganic anions, monocarboxylate anions, and dicarboxylate anions) are major constituents of particulate matter and taken together to their acid and basic precursors are ubiquitous in atmosphere. Water-soluble organic compounds (WSOC) constitute a substantial fraction of atmospheric organic matter, accounting for 10–90% of organic carbon content on fine ambient aerosols depending on locations. Both WSS and WSOC play important roles in global climate change by altering the hygroscopicity of atmospheric aerosols. They can also cause negative effects on human health by increasing the solubility of toxic pollutants. Moreover, some WSOC are allergens, leading to asthma and other diseases [7–9]. Low-molecular-weight carboxylic acids are water-soluble and thus their presence in aerosols enhances the hygroscopic properties of atmospheric particles. These compounds in atmospheric particles may enhance their ability to act as cloud condensation nuclei (CCN) or ice nuclei (IN). They are a major fraction of water-soluble organic compounds (WSOC) in aerosols [10].

WSS or major ions are important source tracers of both anthropogenic (combustible burning, biomass burning, and industrial burning) and biogenic origins (vegetable emission, particle suspension, and sea spray) as well as secondary processes (photochemical reactions and gas-to-particle conversion) which, in turn, contribute to tropospheric acidity, acid rain, CCN formation and climate change [1–3,11,12]. Main removal mechanisms through which these compounds are removed from the atmosphere are dry and wet depositions. In this way, water-soluble ions are transferred

* Corresponding author at: Universidade Federal da Bahia, Instituto de Química, 40170-290, Campus de Ondina, Salvador, BA, Brazil. Tel.: +55 71 32836828; fax: +55 71 32355166.
E-mail address: giseleor@pq.cnpq.br (G.O. da Rocha).

0021-9673/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chroma.2012.08.074

from the atmosphere into other environmental compartments, such as soil, water reservoirs (lakes, rivers, groundwater, oceans, etc.), forests, materials, and others [6,11,13–15]. This transference contributes to nutrient cycling through environmental compartments and, in some cases, may lead to eutrophication [2,16,17].

Considering the relevance of studying WSS and WSOC and the need of improve understanding of the roles these compounds play in issues of atmospheric pollution and human health, it becomes necessary to develop and validate comprehensive analytical methods. Ideally, such an analytical method will have the potential to perform accurate and traceable measurements of the mass concentration of anions and cations in ambient air, as well as the mass fraction of these compounds in PM. This method would be able to provide reliable data sets that could be used to measure the exposure of the general population to these compounds, assess compliance with legislative limits or similar target values, contribute to policy development and assess the effectiveness of abatement strategies. Anion and cation measurements will be soon mandated in the European Union [18] but so far, it seems there is no other initiative by regulatory/environmental agencies to generate policies for tracing anions and cations (or WSS and WSOC) in PM in the near future.

Ion chromatography (IC) and capillary electrophoresis (CE) are currently the main analytical methods used for determination of anions and cations in PM [6,18,19]. IC is the more popular technique of the two. Both the techniques are suitable for determination of cations and anions. However, a substantial number of studies have measured preferentially inorganic anions (such as Cl^-, NO_3^-, PO_4^{3-}, and SO_4^{2-}) [9,15,17,18,20] and when some others have also considered carboxylate anions, only formate and acetate have been included [2,3,6]. Moreover many of these cited reports, when is not available an ion chromatograph with a cation module, Ca^{2+}, Na^+, K^+, and Mg^{2+} have been measured by flame atomic absorption spectrometry (FAAS) [17,21]. However, when using FAAS, NH_4^+, which is a useful source tracer, is not measured. In our opinion, this analytical omission is most likely caused by an instrumental difficulty that makes it difficult to enable simultaneous measurements of inorganic anions, mono-, di-, and tricarboxylate anions in a single run. This limitation prevents a wider study of this class of compounds in PM samples and, consequently, a deeper approach to their human health and atmospheric concerns.

Alternatively, when analyzing normal, branched, bifunctional or aromatic carboxylic acids with longer carbon chain (C_1–C_{10}), other analytical methods such as GC-FID or GC–MS [22–26]. When these methods are used, the carboxylic acid content must be derivatizated prior to analysis by a GC instrument equipped with DB1 or DB5 capillary column. Many homologous series of carboxylic acids are determined as either one of the following derivatives: BF3/n-butanol, α,p-dibromoacetophenone, and/or BSTFBA. Such derivatives when allied to a mass spectrometer, chemical structure elucidation can be done. The disadvantages of GC methods are primarily associated with sample preparation required by these methods. This sample preparation involves several complicated steps, including sample extraction with pure water, concentrations of the obtained extracts, and derivatization of acids to esters [26]. Furthermore, it is not possible to analyze inorganic anions and crustal cations simultaneously in the same run. If there also is interest in determining both inorganic anions and crustal cations it still is necessary to perform capillary electrophoresis, ion chromatography or flame atomic absorption spectrometry (for crustal cations only) afterwards. Ion chromatography, however, has the potential to determine inorganic cations and anions as well as mono-, di-, and tricarboxylates in a single run and does not require sample derivatization or complicated and time-consuming sample extractions. Moreover, minimizing sample manipulation serves for decreasing the possibility to occur sample contamination. Additionally, for analyzes in which sample size is a concern, having an analytical method that requires a smaller aliquot of sample to determine of a wide range of species in a simpler and more comprehensive way would be more suitable. However, since ion chromatography/conductance detection can analyze only ionic or ionizable and hydrophilic species, results for carboxylate species are limited to short chain carboxylate ions (up to C_5). For carboxylates with longer carbon chains, GC-FID or GC–MS are more appropriate techniques. Depending on the main objective of the study, the investigator may choose among the methods GC-FID, GC–MS, CE or ion chromatography. All of them have both advantages and disadvantages, and there will be situations they could be used in a complementary manner.

The goal of the present study was to develop, optimize and validate an ion chromatographic method for simultaneous determination of 14 anions (fluoride, lactate, acetate, propionate, formate, butyrate, pyruvate, chloride, nitrate, succinate, sulfate, oxalate, phosphate, and citrate) and 6 cations (Li^+, Na^+, K^+, NH_4^+, Mg^{2+}, and Ca^{2+}) in PM samples. Validation was done following internationally accepted criteria of analytical figures such as linearity, repeatability, selectivity, precision, accuracy, limit of detection, limit of quantification, ruggedness, and application to real samples.

2. Experimental

2.1. Chemicals, eluents, and analytical standards

All chemical solutions, standard solutions, and eluents utilized in this work were prepared using ultrapure water from Millipore purification system (Millipore Corporation, USA) with resistivity higher than 18.2 MΩ cm^{-1} and conductivity of 0.054 μS cm^{-1} at 25 °C. Stock solutions were made for anions (fluoride, lactate, acetate, propionate, formate, butyrate, pyruvate, chloride, nitrate, succinate, sulfate, oxalate, and phosphate) and cations (lithium, sodium, potassium, ammonium, magnesium, and calcium) considered in this study. Each individual stock solution of 1000 mg L^{-1} were made from either sodium, potassium, ammonium or chloride salts of studied ions possessing the ACS and/or chromatographic purity grades, purchased from Sigma–Aldrich (USA), Merck (Germany) or J.T. Baker (USA). After preparation, stock solutions were kept in freezer for 3 months. Fresh analytical standard mixes were prepared via successive dilutions of each individual stock solution. Eight to ten concentration levels of analytical standards ranged from 25 μg L^{-1} to 1000 μ L^{-1} for external calibration analytical curve. Eluents used in this study were sulfuric acid (ACS and chromatographic grade, J.T. Baker, USA) for cation analyses and potassium hydroxide/ultrapure water (automatic generated by Dionex System, Eluent Generator Cartridge, USA).

The eluents used in this study were the following: (i) 17.5 mmol L^{-1} sulfuric acid (ACS and chromatographic grade, J.T. Baker, USA) for cation analyses, and (ii) potassium hydroxide/ultrapure water for anion analyses. In the latter case, potassium hydroxide solution was automatically generated from KOH cartridge by eluent generator system from Dionex Ion Chromatograph. KOH dilution was done with ultrapure water from Millipore system in an eluent bottle.

2.2. Analytical equipment

A dual-system ion chromatograph–conductance detector equipped with a cation isocratic module (model ICS 1100), an anion gradient module (model ICS 2100), an AS-DV 40 autosampler, and an eluent regenerator system (RFIC-ER) was purchased from Dionex Corporation (USA) and was used in this study. This system enables simultaneous injection in both cation and anion modules

and perform determination of cations and anions in the same time. Cations and anions determinations were done by using IonPac AS11-HC anion analytical column (2 mm × 250 mm, Dionex, USA), IonPac AG11-HC anion guard column (2 mm × 50 mm, Dionex, USA), IonPac CS16 cation analytical column (3 mm × 250 mm, Dionex, USA), IonPac CS16 cation guard column (3 mm × 50 mm, Dionex, USA), anion self-regenerating suppressor (ASRS-300, 2 mm membrane thickness, Dionex, USA) and cation self-regeneration suppressor (CSRS, 2 mm membrane thickness, Dionex, USA), and KOH cartridge/eluent generator system (Dionex, USA).

2.3. Analytical method development, optimization and validation

Method development and optimization were done by univariate procedure. Validation was achieved following recommendations from IUPAC. In this way, validation method was done by obtention of analytical figures such as linearity, calibration, sample matrix effect, repeatability, selectivity, precision, accuracy, limit of detection, limit of quantification, ruggedness, and application to real samples [18–21]. The method was successfully applied to real atmospheric PM samples.

2.4. Atmospheric sample collection and sample extraction

We collected PM1 and PM2.5 samples ($n = 3$ for each size fraction, at sea level) on Aratu Navy Base (12°48′19″S and 38°29′54″W), located about 35 km away from Salvador City, Northeastern Brazil. Both PM1 and PM2.5 samples were collected by using a filter holder equipped with a PTFE filter (47 mm diameter, 1 μm pore size, Sartorius, Germany) coupled to cyclone-type sampler with inlets that established an appropriate particle size cutoff. Collection time was 24 h under a flow rate of 10 L min^{-1}, between 16th and 20th September 2010. After collection, filters were folded in half face to face, placed in a plastic bag, transported cool to the laboratory and stored in a freezer (−4 °C) prior to analysis to prevent the evaporation of volatile components. These were the samples used in this study for validation of our analytical methodology.

To prepare PM samples for analysis, one-fourth of each filter was placed in a 5 mL screwed cap vial and was extracted with 2 mL 2% (v/v) isopropanol (analytical grade, J.T. Baker, USA) and ultrapure water under 10 min mechanical agitation at room temperature. Extracts were filtered through Millex units (filtration units of regenerated cellulose, 0.22 μm pore size, 15 mm diameter, Millipore, USA) [2,3]. After filtration, these sample extracts were injected in the ion chromatograph.

3. Results and discussion

3.1. Development and optimization of chromatographic method

Best conditions for method development adjustments were done under univariate optimization protocols. Firstly, for anions separation, since no conditions for an isocratic separation were found, several gradient programs were evaluated. The best conditions for inorganic, mono-, di-, and tri- carboxylate anions together in a single run was obtained under the following eluent program: in the beginning of the run until 14 min, KOH was set at 0.6 mmol L^{-1}, between 14 and 20 min KOH varied from 0.6 mmol L^{-1} to 15 mmol L^{-1} then raised to 38 mmol L^{-1} during 20–32 min and finally returned to 0.6 mmol L^{-1} in 3 min. The total running time was 35 min (Fig. 1). Eluent flow rate was set at 0.38 mL min^{-1} as well as suppressor current was 36 mA. The column temperature was 36 °C. Injection volume was set at 25 μL. The proposed method was found to produce a satisfactory separation and quantification of the following anions (in elution order):

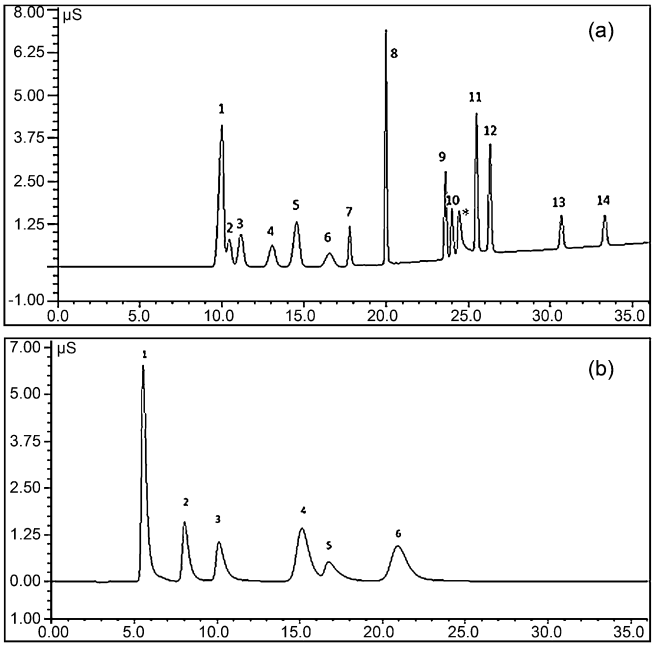

Fig. 1. 25 μg L^{-1} major ions standard solution chromatograms. a: Anion chromatogram were peak are: (1) F^- (tr = 10.02 min), (2) lactate (tr = 10.54 min), (3) CH_3COO^- (tr = 11.26 min), (4) propionate (tr = 13.21 min), (5) $HCOO^-$ (tr = 14.71 min), (6) n-butyrate (tr = 16.78 min), (7) pyruvate (tr = 17.82 min), (8) Cl^- (tr = 20.00 min), (9) NO_3^- (tr = 23.64 min), (10) succinate (tr = 24.04 min), (11) SO_4^{2-} (tr = 25.55 min), (12) oxalate (tr = 26.37 min), (13) PO_4^{3-} (tr = 30.77 min), (14) citrate (tr = 33.44 min). b: (1) Li^+ (tr = 5.86 min), (2) Na^+ (tr = 8.81 min), (3) NH_4^+ (tr = 11.18 min), (4) K^+ (tr = 17.32 min), (5) Mg^{2+} (tr = 19.29 min), (6) Ca^{2+} (tr = 24.71 min). Peak * is carbonate.

fluoride, lactate, acetate, propionate, formate, n-butyrate, pyruvate, chloride, nitrate, succinate, sulfate, oxalate, phosphate, and citrate.

Secondly, for cation separation, it was possible to use an isocratic eluent method. Suitable separations of the following cations (in elution order) were obtained: Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}. The eluent utilized was sulfuric acid 17.5 mmol L^{-1} at 0.36 mL min^{-1} at room temperature. Suppressor current was set at 43 mA (Fig. 1). Injection volume was set at 25 μL. All cations were eluted in less than 25 min. Since our chromatograph enables an automatic injection into both anion and cation modules, every run was simultaneously done for anions and cations separation. This reduces drastically not only the minimum required sample size, the required time for sample manipulation, the analysis time necessary to quantitate ions but also gives us the opportunity to consider a larger number of samples to obtain a more representative dataset of a given study area. Thus, the proposed method has many very attractive advantages over other chromatographic (or electrophoretic) methods for the chemical characterization of PM. This may represent a good advance for atmospheric or environmental research.

After identifying the optimal separation conditions for 20 ions by ion chromatography with conductance detection, in order to guarantee analytical quality of results, we have established the analytical parameters such as linearity, calibration, sample matrix effect, repeatability, selectivity, precision, accuracy, limit of detection, limit of quantification, ruggedness, and application to real samples [27–30].

3.2. Establishment of analytical parameters

3.2.1. Selectivity

A very important criterion of an analytical method is its capability to deliver signals that are free from interferences and give

Table 1
Data set including analytical curve, linearity and linear range of this study.

ions	Analytical curve ($y = ax + b$)	linearity (R^2)	Linear range ($\mu g\,L^{-1}$)
F^-	$y = 0.0014x - 0.0087$	0.9998	5–5000
Lactate	$y = 0.0002x - 0.0027$	0.9977	25–1000
CH_3COO^-	$y = 0.0003x - 0.0013$	0.9997	25–1000
Propionate	$y = 0.0003x - 0.0023$	0.9922	25–5000
$HCOO^-$	$y = 0.0006x - 0.0059$	0.9995	25–1000
n-Butyrate	$y = 0.0002x - 0.0063$	0.9974	100–5000
Pyruvate	$y = 0.0002x - 0.0032$	0.9994	25–1000
Cl^-	$y = 0.0008x + 0.0025$	0.9999	1–5000
NO_3^-	$y = 0.0004x - 0.0066$	0.9987	25–1000
Succinate	$y = 0.0002x - 0.0025$	0.9997	25–1000
SO_4^{2-}	$y = 0.0005x - 0.0026$	0.9994	25–1000
Oxalate	$y = 0.0005x - 0.0037$	0.9997	25–5000
PO_4^{3-}	$y = 0.0002x + 0.0011$	0.9956	25–5000
Citrate	$y = 0.0002x - 0.0015$	0.9995	25–1000
Li^+	$y = 0.0023x - 0.0186$	0.9998	5–5000
Na^+	$y = 0.0007x + 0.0385$	0.9965	1–5000
NH_4^+	$y = 0.0005x + 0.0227$	0.9946	25–5000
K^+	$y = 0.0004x - 0.0064$	0.9996	50–5000
Mg^{2+}	$y = 0.0004x - 0.0092$	0.9962	25–5000
Ca^+	$y = 0.0006x + 0.0922$	0.9955	1–5000

Table 2
LOD and LOQ found in this study for atmospheric samples.

Ions	LOD[a] ($\mu g\,L^{-1}$)	LOQ[a] ($\mu g\,L^{-1}$)	LOD[b] ($pg\,m^{-3}$)	LOQ[b] ($pg\,m^{-3}$)
F^-	7.4	25	30	80
Lactate	22	74	80	250
CH_3COO^-	7.7	26	30	90
Propionate	11	36	40	120
$HCOO^-$	12	41	50	140
n-Butyrate	13	43	50	140
Pyruvate	18	59	70	200
Cl^-	8.5	28	30	90
NO_3^-	23	78	90	260
Succinate	13	43	50	140
SO_4^{2-}	13	43	50	140
Oxalate	17	55	60	180
PO_4^{3-}	25	83	130	400
Citrate	12	39	40	130
Li^+	5.0	17	3.0	10
Na^+	5.7	19	20	70
NH_4^+	10	33	20	60
K^+	7.9	27	20	70
Mg^{2+}	7.5	25	20	70
Ca^+	21	64	80	230

[a] LOD and LOQ calculated from analytical curve.
[b] LOD and LOQ calculated considering a nominal sampled air volume of 7.2 m^3.

"true results". The ability to discriminate between the analyte and interfering compounds in a complex mixture or sample matrix is called selectivity [30–32]. In this study selectivity was evaluated by observing if there is any interfering peak around analyte peak when comparing chromatograms of a real sample matrix absent of analytes and a real sample enriched with analyte standard solution. In this way, we were able to conclude there are no interfering peaks eluting in the vicinity of the analyte peaks. Thus, we inferred that the method proposed was selective for the 20 ions of interest.

3.2.2. Response function, linearity and linear range

The response function of an analytical procedure is, within the range, the existing relationship between the response (signal) and the concentration (quantity) of the analyte in the sample. In turn, linearity is its ability within a definite range, to obtain results directly proportional to the concentrations of the analyte in the sample. Also, the lower and higher limits of the analytical curse is defined as linear range [27,28,33]. For acquisition of analytical curves, 1000 $mg\,L^{-1}$ stock solutions were made for anions (fluoride, lactate, acetate, propionate, formate, butyrate, pyruvate, chloride, nitrate, succinate, sulfate, oxalate, phosphate, and citrate) and cations (lithium, sodium, potassium, ammonium, magnesium, and calcium). In sequence, fresh analytical standard mixes were made by successive dilutions. Between 7 and 15 concentration levels of analytical standards ranged from 1 $\mu g\,L^{-1}$ to 5000 $\mu g\,L^{-1}$ for external calibration analytical curve. Each standard solution was injected three times in the ion chromatograph. The resulting analytical curves (assessed by line equation format as $y = ax + b$, where "a" is the angular coefficient and "b" is the linear coefficient of the curve for a given ion), linearity (assessed by R^2 of the curve) and linear range are included in Table 1. In this study we considered evidence of ideal data fit whenever R^2 is equal or above 0.9900. For all ions, R^2 were above 0.99 that indicates good linearity. Linear range was between 1 and 5000 $\mu g\,L^{-1}$, depending on which ion is considered.

3.2.3. Test for matrix sample effect

In this study the matrix sample effect was evaluated by comparing the angular coefficients (a) of two linear regression curves, which were acquired both with and without standard addition. The first curve was done with six different concentration levels of ion standards added to particulate matter samples ($a_{standard+sample}$) while the second curve was done with aqueous ion standard solution ($a_{standard}$). When the slopes of both curves is equal or very close one to another, $a_{standard+sample}/a_{standard}$ tends to approach 1, meaning that there is no matrix effect. The developed method from this study is not considered to be susceptible to matrix effect because $a_{standard+sample}/a_{standard}$ values were near unity (from 1.0 for CH_3COO^- to 1.2 for Mg^{2+}). Additionally there is no need to use standard addition method (which is time-consuming) for quantifying ions in particulate matter samples.

3.2.4. Limit of detection and limit of quantification

The concept of limit of detection (LOD) and limit of quantification (LOQ) may vary according to working area. The notion of LOD of an analyte may be described as that concentration which gives an instrumental signal significantly different from "blank" or "background" signal. LOQ is the smallest value of analyte that can be determined quantitatively, with a certain limit of confidence. Below the value determined for LOQ, measurements do not represent sufficient confidence for quantification [32]. According to Ribani et al. [32] an alternative to find LOD and LOQ of a method is to calculate them based on response SD-to-inclination of analytical curve rate, LOD = $3s/a$ and LOQ = $10s/a$, where 's' is the SD of linear coefficient and 'a' is the angular coefficient (inclination) from analytical curve (see also [34–37]). In our study, LOD ranged 5.0–25 $\mu g\,L^{-1}$ (Li^+ and PO_4^{3+}, respectively) and LOQ was within 17–83 $\mu g\,L^{-1}$ (Li^+ and PO_4^{3+}, respectively) (Table 2). Considering a nominal sampled air volume of 7.2 m^3, LOD and LOQ were in the mid- to sub-$pg\,m^{-3}$ range for most species. For instance, LOD ranged 3.0–130 $pg\,m^{-3}$ and LOQ was within 10–400 $pg\,m^{-3}$ (Li^+ and PO_4^{3+}, respectively, for both cases). To our knowledge, there is no other published method able to reach such a low LOD and LOQ values ($pg\,m^{-3}$ range) for a simultaneous analysis of 20 ions. This gives us a reliable method to study ions occurrence in PM even from remote areas or near natural conditions of an ecosystem.

3.2.5. Precision

Precision is the closeness of agreement between independent test results obtained under stipulated conditions. It is usually specified in terms of relative standard deviation (RSD). Precision may be considered at three levels: repeatability, intermediate precision and reproducibility [28,36,38,39].

Repeatability or intra-day precision expresses the precision under the same operating conditions (same procedure, same analyst, same instrument used at same conditions, same place,

Table 3
Repeatability (intra-day precision) expressed as RSD (%).

Species	50 μg L^{-1}		500 μg L^{-1}		1000 μg L^{-1}	
	tr	Area	tr	Area	tr	Area
F^-	0.16	0.72	0.16	0.38	0.14	0.14
Lactate	0.17	7.52	0.15	1.51	0.13	2.81
CH_3COO^-	0.16	0.75	0.15	1.04	0.13	2.89
Propionate	0.14	2.35	0.14	1.27	0.14	0.91
$HCOO^-$	0.15	1.17	0.14	1.77	0.15	6.63
n-Butyrate	0.14	4.17	0.12	2.72	0.14	1.91
Pyruvate	nd[a]	nd	0.05	2.17	0.04	5.52
Cl^-	0.02	4.55	0.03	0.24	0.02	0.18
NO_3^-	0.02	1.53	0.02	0.40	0.03	6.22
Succinate	0.01	0.5	0.02	1.86	0.02	4.84
SO_4^{2-}	0.01	3.49	0.02	4.40	0.02	2.44
Oxalate	0.02	1.69	0.02	0.30	0.02	0.36
PO_4^{3-}	0.01	8.53	0.02	1.14	0.01	0.47
Citrate	0.01	2.59	0.03	1.29	0.01	2.98
Li^+	0.16	1.25	0.06	0.48	0.09	0.39
Na^+	0.19	5.39	0.10	0.88	0.06	1.13
NH_4^+	0.18	2.85	0.09	1.87	0.04	1.69
K^+	0.31	5.61	0.10	1.83	0.11	3.07
Mg^{2+}	0.29	11.0	0.21	2.85	0.06	2.37
Ca^+	0.10	17.8	0.11	8.95	0.09	11.3

[a] nd means to be below LOQ.

repetitions during a short time looping). In this study, repeatability was evaluated for retention time and detector response (as measured by peak area) with standard solution at 50, 500 and 1000 μg L^{-1}, each one injected in quintuplicate during the same day and expressed as RSD (Table 3). Intermediate precision or inter-day precision expresses within-days variations. For approach that, also in regarding of retention time and peak area, we used standard solutions at 3 concentration levels – 50, 500 and 1000 μg L^{-1}, each one injected in triplicate for four consecutive days. Intermediate precision data, expressed as RSD, is available in Table 4. To assess reproducibility is necessary to establish inter-laboratory protocols. This test was not done in this study.

For retention time, all measurements were below 2% (for both repeatability and intermediate precision) for every ion considered in this study. If considering peak area, we found RSD below 20% in both kinds of precision tests. Taking into account that a RSD up to 20% is acceptable for trace analysis of complex matrices, this method could be considered quite precise for major ions quantification in PM samples.

Table 4
Intermediate precision (inter-day precision) expressed as RSD (%).

Species	50 μg L^{-1}		500 μg L^{-1}		1000 μg L^{-1}	
	tr	Area	tr	Area	tr	Area
F^-	0.28	0.26	0.17	0.21	1.52	0.89
Lactate	0.31	2.14	0.16	1.6	1.47	2.59
CH_3COO^-	0.3	10.2	0.15	5.46	1.46	10.9
Propionate	0.33	3.66	0.17	1.58	1.37	2.54
$HCOO^-$	0.33	3.69	0.20	2.83	1.22	16.6
n-Butyrate	0.36	3.98	0.18	4.09	1.34	2.65
Pyruvate	nd[a]	nd	0.08	4.47	0.40	9.03
Cl^-	0.27	4.87	0.05	1.16	0.13	1.98
NO_3^-	0.09	14.4	0.05	0.85	0.06	6.84
Succinate	0.11	17.1	0.04	3.2	0.05	11.3
SO_4^{2-}	0.15	10.7	0.04	3.58	0.05	3.73
Oxalate	0.14	1.74	0.04	0.6	0.05	3.64
PO_4^{3-}	0.11	6.68	0.04	1.28	0.05	4.41
Citrate	0.08	14.8	0.04	3.7	0.05	4.78
Li^+	0.16	1.25	0.06	0.48	0.09	0.39
Na^+	0.19	5.39	0.10	0.88	0.06	1.13
NH_4^+	0.18	2.85	0.09	1.87	0.04	1.69
K^+	0.31	5.61	0.10	1.83	0.11	3.07
Mg^{2+}	0.29	11.0	0.21	2.85	0.06	2.37
Ca^+	0.10	17.8	0.11	8.95	0.09	11.3

[a] nd means to be below LOQ.

Table 5
Recoveries values (%) for PM samples.

Species	300 (μg L^{-1})	500 (μg L^{-1})
F^-	97	95
Lactate	101	104
CH_3COO^-	100	107
Propionate	92	91
$HCOO^-$	95	99
n-Butyrate	93	111
Pyruvate	97	99
Cl^-	123	60
NO_3^-	102	90
Succinate	119	119
SO_4^{2-}	98	65
Oxalate	97	105
PO_4^{3-}	92	102
Citrate	90	88
Li^+	120	100
Na^+	93	86
NH_4^+	96	113
K^+	92	118
Mg^{2+}	90	86
Ca^+	89	79

3.2.6. Accuracy

Because there is no certified reference material (CRM) for major ions in PM samples, accuracy was measured through recovery test. For that, it was transferred to 5 mL screwed cap vials 3 pieces of the same PM filter sample. In the first vial, we transferred the PM filter only. Then, we transferred 10 μL of 300 μg L^{-1} ions standard on PM filter in the second vial. Finally, in the third vial we added 10 μL of 500 μg L^{-1} ions standard on PM filter. In order to favor standard solution impregnating into PM matrix, it was allowed this mixture overnight before extraction. Then, they were extracted by the same procedure done for all samples and analyzed in three replicates each. Recovery levels are listed in Table 5. Recovery ranged from 89% (Ca^{2+}) to 120% (Li^+) at 300 μg L^{-1} standard addition and from 60% (Cl^-) to 119% (succinate) at 500 μg L^{-1} standard addition. Recoveries between 50 and 120% are considered acceptable when measuring trace analytes from complex or environmental matrices. In this way, since our recoveries levels were adequate, the proposed method was found to have good agreement between found and accepted values. Fluctuations or differences between both values (found and accepted) were due to random errors. We believe there are no systematic error contributions.

3.2.7. Ruggedness

Ruggedness of an analytical method is the resistance to have changes in the results produced by an analytical method when minor but deliberate deviations are made from experimental conditions described in the procedure [19]. In the present study, we tested if there were modifications in the detector response towards (i) anion column temperature change (36–39 °C), and (ii) eluent flow rate change (0.36–0.38 mL min^{-1}) (Table 6). Changes in the chosen parameters provoked only minor variations in the detector response (measured in absolute terms). This means that the present method is rugged.

3.2.8. Test with real samples

Initially, it was verified which ions would be found in our target samples to then perform their quantification afterwards. Identification was done by matching retention time of compounds found in the samples to retention time of ions from standard solutions. Some samples were also spiked with ion standard solution in order to verify whether or whether not would have an increase in the ion peak

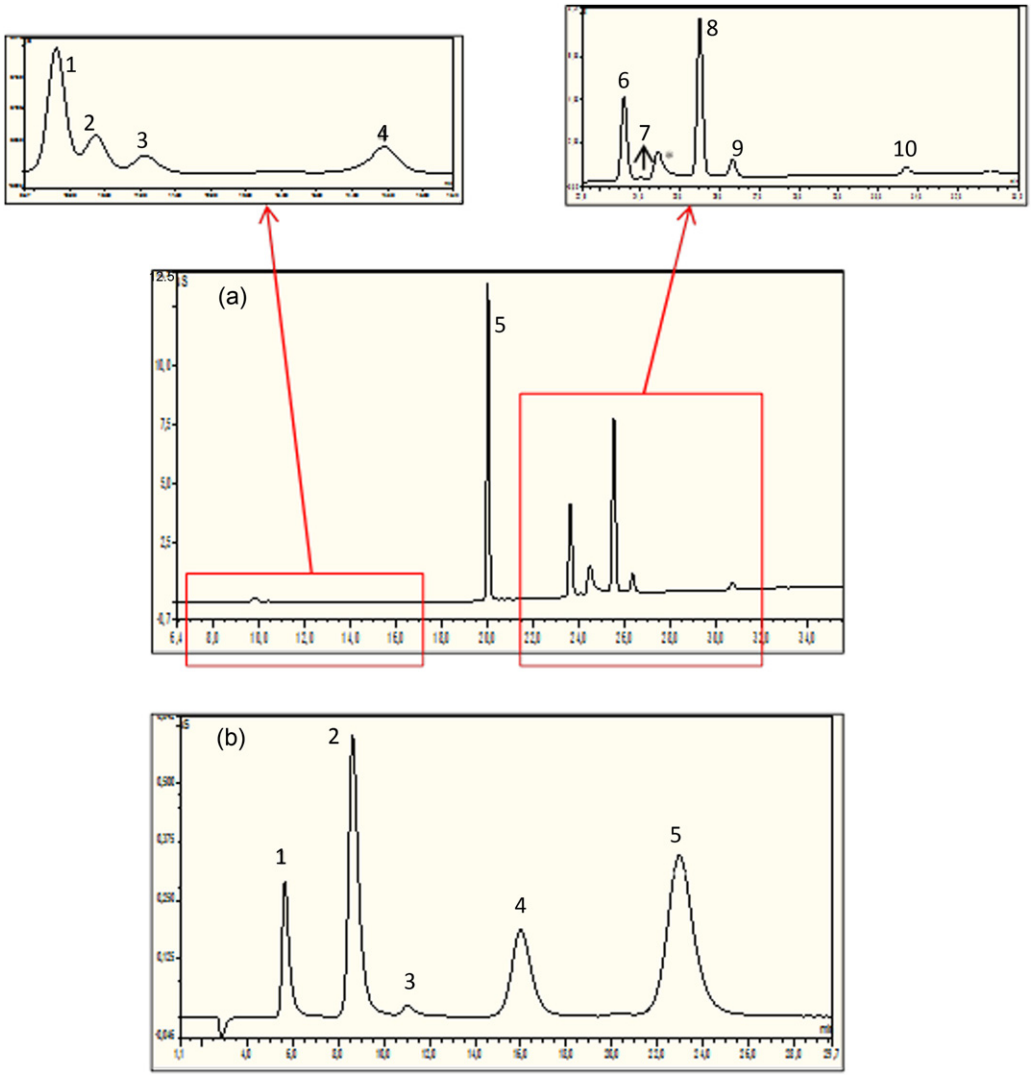

Fig. 2. Chromatograms of PM2.5 real sample. a: (1) F^- (1.2 ng m^{-3}), (2) lactate (6.9 ng m^{-3}), (3) CH_3COO^- (2.6 ng m^{-3}), (4) $HCOO^-$ (6.7 ng m^{-3}), (5) Cl^- (32 ng m^{-3}), (6) NO_3^- (6.6 ng m^{-3}), (7) succinate (0.9 ng m^{-3}), (8) SO_4^{2-} (73 ng m^{-3}), (9) oxalate (3.9 ng m^{-3}), (10) PO_4^{3-} (0.4 ng m^{-3}). b: (1) Na^+ (15 ng m^{-3}), (2) NH_4^+ (0.1 ng m^{-3}), (3) K^+ (0.1 ng m^{-3}), (4) Mg^{2+} (0.7 ng m^{-3}), (5) Ca^{2+} (0.2 ng m^{-3}). Peak * is carbonate.

Table 6
Variation in detector response (μS) caused by changes in some method parameters.

ion	Variation in detector response (μS)	
	Column temp.[a]	Eluent flowrate[b]
F^-	14.9	14.9
Lactate	0.26	0.26
CH_3COO^-	0.36	0.36
Propionate	0.29	0.30
$HCOO^-$	0.57	0.58
n-Butyrate	0.23	0.23
Pyruvate	0.22	0.22
Cl^-	0.87	0.87
NO_3^-	0.43	0.43
Succinate	0.23	0.23
SO_4^{2-}	0.67	0.71
Oxalate	0.57	0.57
PO_4^{3-}	0.22	0.22
Citrate	0.21	0.21
Li^+	23.9	24.3
Na^+	0.83	0.83
NH_4^+	0.58	0.59
K^+	0.73	0.71
Mg^{2+}	0.48	0.47
Ca^+	0.91	0.87

[a] Changes in the anion column temperature between 36 and 39 °C.
[b] Changes in the eluent flow rate between 0.36 and 0.38 mL min^{-1}.

Table 7
Concentration levels (units in ng m^{-3}) found in PM1 and PM2.5 samples from Aratu Navy Base.

ion	PM1 (mean ± SD)[a]	PM2.5 (mean ± SD)[a]
F^-	0.09 ± 0.01	0.09 ± 0.02
Lactate	7.9 ± 2.1	8.6 ± 3.0
CH_3COO^-	1.3 ± 0.5	1.5 ± 0.1
$HCOO^-$	2.3 ± 0.2	2.3 ± 0.2
Cl^-	43 ± 19	34 ± 22
NO_3^-	7.3 ± 1.4	6.7 ± 2.1
Succinate	0.8 ± 0.5	0.5 ± 0.1
SO_4^{2-}	66 ± 3.5	62 ± 9.4
Oxalate	3.6 ± 3.9	3.8 ± 3.0
PO_4^{3-}	29 ± 15	35 ± 9.4
Na^+	4.1 ± 1.5	7.3 ± 1.3
NH_4^+	0.2 ± 0.06	0.06 ± 0.03
K^+	0.2 ± 0.06	0.2 ± 0.03
Mg^{2+}	0.3 ± 0.07	0.2 ± 0.05
Ca^+	0.3 ± 0.01	0.5 ± 0.05

[a] (mean ± SD) states for mean value of atmospheric concentration for each ion ± one standard deviation.

areas from PM1 and PM2.5 samples. Moreover, at every working day comparisons between retention times of sample peaks and analytical standards peaks were performed. Every injection was done in triplicate. Ions quantification was carried out by the method of external calibration curve considering peak area (peak area versus concentration) and linear regression as described in the Experimental. Cations and anions chromatograms found in real samples area available in Fig. 2 and ion concentration levels are in Table 7. Propionate, n-butyrate, pyruvate, and citrate were not found above limit of detection in the samples. All other analytes were found in concentrations levels well above LOD and LOQ. Indeed, we believe we could show the proposed method works accordingly for major ion determination in atmospheric PM matrices.

4. Concluding remarks

The results presented here indicate the proposed method is suitable to simultaneous quantification of inorganic anions monocarboxylate anions, dicarboxylate anions, tricarboxylate anion, and crustal cations in the low pg m^{-3} range in atmospheric PM samples by ion chromatography–conductivity detection. This method is a comprehensive, simple, cheap and reliable procedure to study the ions occurrence in PM even from remote areas or near natural conditions of an ecosystem. Application of this method could potentially be extended to the analysis of other atmospheric samples (such as gas phase and rainwater samples) and environmental samples (for instance, in geochemistry, oceanography, and glaciology).

Acknowledgements

Authors wish to thank Brazilian agencies who have funded this work: CNPq, FAPESB, CAPES, and FINEP as well as the anonymous reviewers that have enormously contributed to the current version of this paper.

References

[1] G.O. da Rocha, A. Franco, A.G. Allen, A.A. Cardoso, J. Geophys. Res. 108 (D7) (2003), http://dx.doi.org/10.1029/2002JD002567.
[2] G.O. da Rocha, A.G. Allen, A.A. Cardoso, Environ. Sci. Technol. 39 (2005) 5293.
[3] A.G. Allen, A.A. Cardoso, G.O. da Rocha, Atmos. Environ. 38 (2004) 5025.
[4] S. Canepari, E. Cardarelli, A. Giuliano, A. Pietrodangelo, Talanta 69 (2006) 581.
[5] G.C. Fang, Y.S. Wu, C.C. Wen, C.K. Lin, S.H. Huang, J.Y. Rau, C.P. Lin, Toxicol. Ind. Health 21 (2005) 259.
[6] A. Fornaro, I.G.R. Gutz, Atmos. Environ. 37 (2003) 117.
[7] G. Wang, C. Chen, J. Li, B. Zhou, M. Xie, S. Hu, K. Kawamura, Y. Chen, Atmos. Environ. 45 (2011) 2473.
[8] G. Wang, K. Kawamura, C. Chen, J. Li, J. Cao, R. Zhang, T. Zhang, S. Liu, Z. Zhao, Environ. Sci. Technol. 46 (2012) 4783.
[9] S. Decesari, M.C. Facchini, S. Fuzzi, G.B. McFiggans, H. Coe, K.N. Bower, Atmos. Environ. 39 (2005) 211.
[10] G. Wang, K. Kawamura, M. Xie, S. Hu, J. Li, B. Zhou, J. Cao, Z. Na, Tellus 63B (2011) 371.
[11] T. Shimamura, M. Iwashita, S. Iijima, M. Shintani, Y. Takaku, Atmos. Environ. 41 (2007) 6999.
[12] A. Chebbi, P. Carlier, Atmos. Environ. 30 (1996) 4233.
[13] P.A. Tanner, P.T. Law, Water Air Soil Pollut. 142 (2003) 279.
[14] G.H. Avery Jr., R.J. Kieber, M. Witt, J.D. Willey, Atmos. Environ. 40 (2006) 1683.
[15] C. Anatolaki, R. Tsitouridou, Atmos. Res. 92 (2009) 100.
[16] L.O. Hedi, Nature 367 (1994) 351.
[17] K.A. Lohse, D. Hope, R. Sponseller, J.O. Allen, N.B. Grimm, Sci. Total Environ. 402 (2008) 95.
[18] R.J.C. Brown, P.R. Edwards, Talanta 80 (2009) 1020.
[19] R.P. Haddad, P. Doble, M. Macka, J. Chromatogr. A (1999) 856.
[20] F.R. Rocha, J.A.F. da Silva, C.L. Lago, A. Fornaro, I.G.R. Gutz, Atmos. Environ. 37 (2003) 105.
[21] M. Trancoso, A. Souza, F. Mouro, M.C. Freitas, S. Almeida, N. Canha, Accredit. Qual. Assur. 17 (2012) 199.
[22] K. Kawamura, Anal. Chem. 65 (1993) 3505.
[23] K. Kawamura, K. Ikushima, Environ. Sci. Technol. 27 (1993) 2227.
[24] K. Kawamura, L.-L. Ng, I.R. Kaplan, Environ. Sci. Technol. 19 (1985) 1082.
[25] K. Kawamura, S. Steinberg, I.R. Kaplan, Atmos. Environ. 30 (1996) 1035.
[26] K. Kawamura, L.A. Barrie, D. Toom-Sauntry, Atmos. Environ. 44 (2010) 5316.
[27] M. Thompson, S.L.R. Ellison, A. Fajgelj, P. Willetts, R. Wood, Pure Appl. Chem. 71 (1999) 337.
[28] M. Thompson, S.L.R. Ellison, R. Wood, Pure Appl. Chem. 74 (2002) 835.
[29] H. Egli, M. Dassenakis, H. Garelick, R. Van Grieken, W.J.G.M. Peijnenburk, L. Klasinc, W. Kordel, N. Priest, T. Tavares, Pure Appl. Chem. 75 (2003) 1097.
[30] J. Vessman, R.I. Stefan, J.F.V. Staden, K. Danzer, W. Lindner, D.T. Burns, A. Fajgelj, H. Müller, Pure Appl. Chem. 73 (2001) 1381.
[31] M. Ribani, C.B.G. Bottoli, C.H. Collins, I.C.S.F. Jardim, L.F.C. Melo, Quim. Nova 27 (2004) 771.
[32] M. Ribani, C.B.G. Bottoli, C.H. Collins, I.C.S.F. Jardim, L.F.C. Melo, J. Chromatogr. A 1156 (2007) 201.
[33] Ph. Hubert, J.J. Nguyen-Huu, B. Boulanger, E. Chapuzet, P. Chiap, N. Cohen, P.A. Compagnon, W. Dewé, M. Feinberg, M. Lallier, M. Laurentie, N. Mercier, G. Muzard, C. Nivet, L. Valat, E. Rozet, J. Pharm. Biomed. Anal. 45 (2007) 70.
[34] W.A. Lopes, G.O. da Rocha, P.A.P. Pereira, F.S. Oliveira, L.S. Carvalho, N.C. Bahia, L.S. Conceição, J.B. de Andrade, J. Sep. Sci. 31 (2008) 1787.
[35] L.C. de Azevedo, M.M. Reis, G.E. Pereira, G.O. da Rocha, L.A. Silva, J.B. de Andrade, J. Sep. Sci. 32 (2009) 3432.
[36] S. Yakkundi, J. Millership, P.D. Collier, M.D. Shields, J. Mcelnaya, J. Pharm. Biomed. Anal. 56 (2011) 1057.
[37] C. Sarazin, N. Delaunay, J.V.J. Varenne, C. Costanza, V. Eudes, J.J. Minet, P. Gareil, J. Chromatogr. A 1217 (2010) 6971.
[38] ICH Harmonised Tripartite Guideline, Validation of Analytical Procedures: Text and Methodology Q2(R1), 2005.
[39] M. Iammarino, A. Di Taranto, M. Muscarella, D. Nardiello, C. Palermo, D. Centonze, Anal. Chim. Acta 672 (2010) 61.