FULL PAPER

# Development of a Methodology for Determining Major Ions in Samples of Atmospheric Particulate Matter by Ion Chromatography

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## Abstract:

Countless deleterious effects on human health and the environment are promoted by the action of air pollutants. Thus, it is necessary the development of analytical methods to identify and quantify efficiently ions present in atmospheric particulate matter. This study proposes a new analytical methodology for simultaneous quantification of 12 organic ions (Lactate, Acetate, Propionate, Formate, Butyrate, Methanesulfonate, Pyruvate, Monochloroacetate, Trifluoroacetate, Succinate, Oxalate and Citrate), 12 inorganic anions (fluoride, bromate, chloride, nitrite, bromide, nitrate, sulfite, sulfate, tungstade, molybdate, phosphate and chromate) and 7 cations (lithium, sodium, ammonium, potassium, magnesium, calcium and strontium) using ion chromatography coupled to conductivity detection. The optimization of the proposed method was performed univariate and validation was done according to IUPAC recommendations; LOD and LOQ varied between 12 to 114 pg m$^{-3}$ and 35 to 342 pg m$^{-3}$ respectively, showing recovery values between 89% to 109% and R$^2$ between 0.9979 and 0.9999 for the 31 main ions studied. Ions were successfully determined in environmental samples of particulate material in the 10 μm and 2.5 μm fractions. This method was considered a comprehensive, accurate, fast and robust procedure for the study of ions in samples of atmospheric particulate matter.

**Keywords:** ion chromatography; environmental samples; major water-soluble ions; particulate matter

## 1. Introduction

Atmospheric particulate matter (PM), also known as aerosol, is usually defined as a suspension of solids and liquids in the atmosphere [1]. These fine particles, of fractions with aerodynamic diameters less than 2.5 μm, exert a complex influence on the planet's climate system and on human health [2]. The PM can be carried by air currents over long distances and, according to their aerodynamic diameter, can penetrate the lung alveoli and cause serious public health problems [3].

PM is composed of several species such as organic and elemental carbon, organic compounds, trace elements, organic and inorganic acids and major ions [4] and can be derived from various sources of anthropogenic and / or biogenic origin [5, 6]. They can be issued directly as primary particles emanating from combustion processes, vehicle and industrial emissions or secondary route from gaseous

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precursors (NH$_3$, SO$_x$ e NO$_x$) forming rich particles SO$_4^{2-}$, NO$_3^-$, NH$_4^+$ [7], apart from natural sources such as soil dust resuspension, sea spray, natural fires, plant metabolism, pollen, bacteria, viruses and volcanic activity [8].

The concentration of PM is directly linked to the global climatic imbalance, changing the amount of solar radiation received and the terrestrial radiation coming out [9, 10]. In recent decades, increasing attention has been given to the negative consequences of increasing PM in the environment [11]. The World Health Organization (WHO) estimates that exposure to air pollution has caused about 7 million deaths worldwide in 2012, disease consequences caused by many types of cancer, cardiovascular and respiratory diseases and allergies, asthma, pulmonary emphysema, cardiopulmonary morbidity and reduced life expectancy [12, 13].

The major ions can be found both in the gas phase as PM. These species are ubiquitous in the atmosphere and are important tracers of anthropic sources (burning fuel, burning biomass and industrial emissions) [14] and biogenic (emission by the plant, particle resuspension, marine emission) [15] and secondary processes of interconversion (photochemical reactions and gas-particle conversion [16–19]. In Brazil, studies carried out in several regions, it has shown that the main sources of major ions in the PM were the industrial, vehicle emissions, biomass burning and natural fires [20, 21].

Among the various components of atmospheric particulate matter, water-soluble ions have stood out for being ubiquitous substances in the atmosphere [22]. These ions can be used as markers of anthropogenic sources, including fuel (acetate, sulfate, succinate) and biomass burning (succinate, oxalate), industrial (ammonium, sulfate) [23] and biogenic emissions by plants (formate) [24]. Moreover, the resuspension of particles and the marine environment (calcium, magnesium, sodium) [25] added to secondary processes of interconversion, photochemical reactions (formate, succinate) and conversion of gaseous particles (sulfate, nitrate) can be identified through water-soluble detection [26].

The characterization of these chemical components in PM has become important in the assessment of climate change, the effects on human health and the ecosystem. Therefore, the need for the quality of chemical measurements, through their comparability, traceability and reliability, is being increasingly recognized and demanded [27]. In this context, ion chromatography (IC) is presented as an alternative technique to determine these images.

IC is a well-established method with increasing use for analysis in water and atmospheric air quality control procedures [28, 29]. Its high selectivity, robustness and sensitivity allows the determination of inorganic anions and cations, as well as organic substances that may exist in ionic form [30, 31]. In many cases, it has replaced conventional wet chemical methods, which are laborious, time-consuming, difficult to automate, limited precision and occasionally, susceptible to interference [32, 33].

The objective of this study was to develop, optimize and validate an ion chromatographic method for the simultaneous determination of 12 organic ion (lactate, acetate, propionate, formate, butyrate, methanesulfonate, pyruvate, monochloroacetate, trifluoroacetate, succinate, oxalate and citrate), 12 inorganic anions (fluoride, bromate, chloride, nitrite, bromide, nitrate, sulfite, sulfate, tungstade, molybdate, phosphate and chromate) and cations (lithium, sodium, ammonium, potassium, magnesium, calcium and strontium) in PM samples using IC - conductivity detection. The validation was performed according to internationally accepted criteria for analytical figures, such as linearity, repeatability, selectivity, precision, accuracy, limit of detection, limit of quantification, robustness and application in real samples.

## 2. Results and Discussion

### 2.1 Development and optimization of chromatographic method

The method was developed and optimized by a univariate procedure. The optimal conditions for the method are: (*i*) anion gradient: initial KOH concentration of 1.10 mmol L$^{-1}$ up to 7.0 min. In the first stage, rising to 9.0 mmol L$^{-1}$ in 13.0 min. in the second stage, going up to 16.0 mmol L$^{-1}$ in 20.0 min. in the third stage, rising to 20.0 mmol L$^{-1}$ in 27.0 min. in the fourth stage up to 36.0 mmol L$^{-1}$ in 37.0 min. in the fifth step in a flow of 0.38 mL min$^{-1}$ and a suppression current of 38 mA; (*ii*) cation: 25 mmol L$^{-1}$ H$_2$SO$_4$ solution was used in

183

*Orbital: Electron. J. Chem. 12 (4): 182-192, 2020*

isocratic mode, but with an initial flow of 0.36 mL$^{-1}$ up to 16.0 min, rising to 0.5 mL$^{-1}$ up to 17 min. remaining up to 37 min. with a suppression current of 74 mA the injection volume of the loop is 50 µL for both channels. Under these conditions, it was possible to determine the 31 ions injected simultaneously in 37 minutes of the analysis.

### 2.2 Validation of the analytical method

Validation was performed according to recommendations from the International Union of Pure and Applied Chemistry (IUPAC). Thus, the validation of the method was made using figures of merit such as selectivity, linearity, limits of detection, limits of quantification, precision, accuracy, ruggedness, matrix effect in the sample and application in real samples [34, 35].

### 2.3 Selectivity

According to IUPAC, selectivity is the degree to which the method can accurately quantify an analyte in the presence of interfering. Ideally, selectivity should be assessed for any substantial interference that it may be. Therefore, selectivity can also be defined as the ability of a method to discriminate between the analyte and the interfering species in a complex matrix sample or mixture [36]. In this context, it was possible to see in the chromatograms (Fig. 1), the determination of 24 species of organic and inorganic anions (Fig. 1a) and 7 cations (Fig. 1b), with no interfering peaks in the chromatographic run being observed. Thus, the proposed method was selective for the 31 ions of interest.
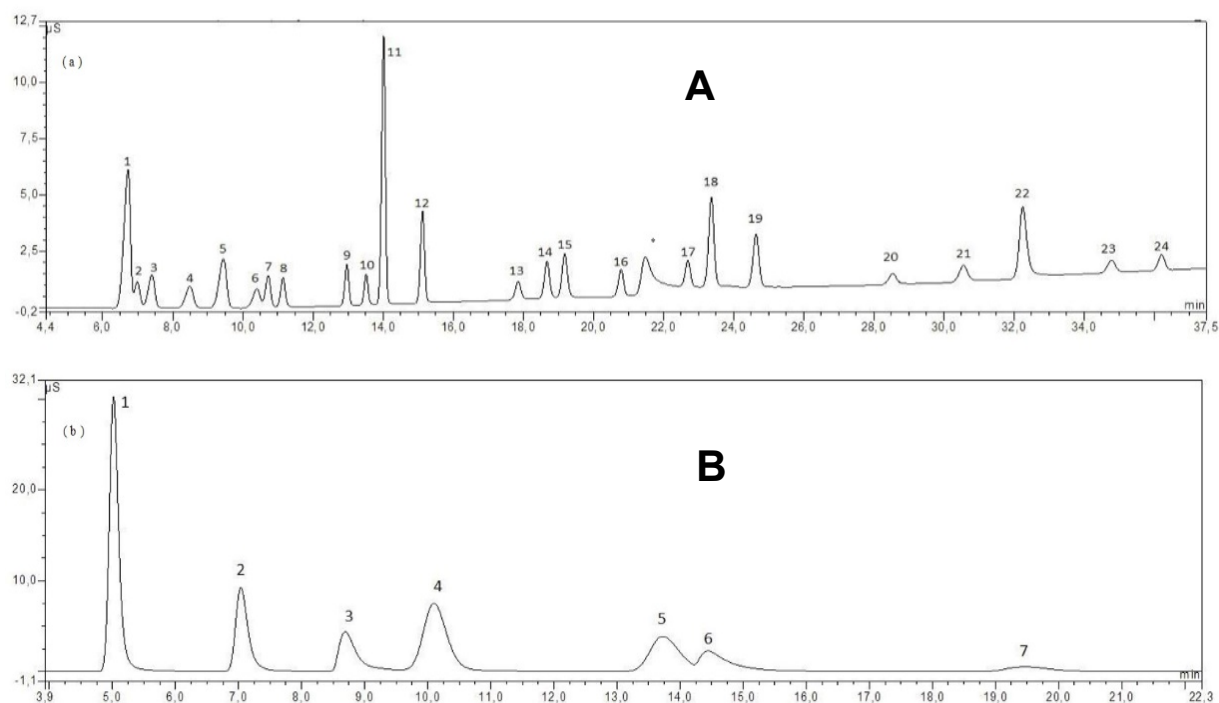


**Figure 1.** Ions in a 500 µg L$^{-1}$ standard solution. (a) Chromatogram of the anions, the numbered peaks are as follows: (1) fluoride (6.68 min), (2) lactate (6.95 min), (3) acetate (7.45 min), (4) propionate (8.48 min), (5) formate (9.57min), (6) butyrate (10.48 min), (7) methanesulfonate (10.78 min), (8) pyruvate (11.29 min), (9) monochloroacetate (13.07 min), (10) bromate (13.62 min), (11) chloride (14.10 min), (12) nitrite (15.22 min), (13) trifluoroacetate (17.95 min), (14) bromide (18.78 min), (15) nitrate (19.28 min), (16) succinate (20.78 min), (17) sulfite (22.70 min), (18) sulfate (23.45 min), (19) oxalate (24.73 min), (20) tungstate (28.64 min), (21) molybdate (30.66 min), (22) phosphate (32.40 min), (23) chromate (34.91 min), (24) citrate (36.33 min). (b): (1) lithium (5.10 min), (2) sodium (7.13 min), (3) ammonium (8.81 min), (4) potassium (10.23 min), (5) magnesium (13.87 min), (6) calcium (14.62 min), (7) strontium (19.54 min).

184

*Orbital: Electron. J. Chem. 12 (4): 182-192, 2020*

### 2.4 Linearity, analytical curve and linear range

Analytical curves were made at concentrations between 0.5 and 500 µg L$^{-1}$ using stock solutions with concentrations of 1000 mg L$^{-1}$ for the fluoride, lactate, acetate, propionate, formate, butyrate, methanesulfonate, pyruvate, monochloroacetate, bromate, chloride, nitrite, trifluoroacetate, bromide, nitrate, succinate, sulfite, sulfate, oxalate, tungstate, molybdate, phosphate, chromate, citrate, lithium, sodium, ammonium, potassium, magnesium, calcium and strontium. The curves found in this study respect the order of linearity described by the formula y = ax + b for each ion. The analytical curves obtained showed linearities within the permitted limits, represented by R$^2$, between 0.9979 and 0.9999 for the 31 ions studied. According to IUPAC curves with 0.9000 and 0.9900 respectively are considered to be of good linearity. The linear working range was established between 0.5 and 2000 µg L$^{-1}$, shown in Table 1.

**Table 1.** Results for the linearity parameters of the proposed method.

| Species | Analytical Curve | Linearity | Linear Range (µg L$^{-1}$) | n |
|---|---|---|---|---|
| Fluoride | y = 0.0037x – 0.0062 | R² = 0.9999 | 1 - 1000 | 9 |
| Lactate | y = 0.0005x – 0.0007 | R² = 0.9996 | 1 - 1500 | 9 |
| Acetate | y = 0.0007x + 0.0037 | R² = 0.9994 | 3 - 1500 | 9 |
| Propionate | y = 0.0006x + 0.0011 | R² = 0.9992 | 3 - 1500 | 9 |
| Formate | y = 0.0013x + 0.0001 | R² = 0.9998 | 1 - 1500 | 9 |
| Butyrate | y = 0.0005x – 0.0007 | R² = 0.9994 | 7 - 1000 | 9 |
| Methanesulfonate | y = 0.0006x – 0.0031 | R² = 0.9997 | 3 - 1500 | 9 |
| Pyruvate | y = 0.0005x – 0.0021 | R² = 0.9996 | 3 - 1500 | 9 |
| Monochloroacetate | y = 0.0006x – 0.0033 | R² = 0.9995 | 3 - 1500 | 9 |
| Bromate | y = 0.0004x – 0.0024 | R² = 0.9985 | 3 - 1500 | 9 |
| Chloride | y = 0.0018x – 0.0047 | R² = 0.9995 | 1 - 2500 | 9 |
| Nitrite | y = 0.0013x – 0.0079 | R² = 0.9995 | 7 - 1000 | 9 |
| Trifluoroacetate | y = 0.0003x – 0.0021 | R² = 0.9986 | 3 - 1500 | 9 |
| Bromide | y = 0.0007x – 0.0052 | R² = 0.9979 | 3 - 1500 | 9 |
| Nitrate | y = 0.0008x – 0.0059 | R² = 0.9995 | 3 - 2000 | 9 |
| Succinate | y = 0.0005x – 0.0015 | R² = 0.9999 | 3 - 1500 | 9 |
| Sulfite | y = 0.0003x – 0.0018 | R² = 0.9994 | 3 - 1500 | 7 |
| Sulfate | y = 0.001x – 0.00131 | R² = 0.9987 | 1 - 1500 | 9 |
| Oxalate | y = 0.001x – 0.00281 | R² = 0.9988 | 1 - 1500 | 9 |
| Tungstate | y = 0.0002x – 0.0007 | R² = 0.9993 | 7 - 2500 | 9 |
| Molybdate | y = 0.0005x – 0.0027 | R² = 0.9993 | 7 - 2500 | 9 |
| Phosphate | y = 0.0004x – 0.0007 | R² = 0.9992 | 3 - 2500 | 9 |
| Chromate | y = 0.0003x – 0.0013 | R² = 0.9993 | 7 - 2000 | 9 |
| Citrate | y = 0.0003x – 0.0011 | R² = 0.9997 | 7 - 2000 | 9 |
| Lithium | y = 0.0033x – 0.0001 | R² = 0.9997 | 1 - 1500 | 9 |
| Sodium | y = 0.0011x + 0.0065 | R² = 0.9997 | 1 - 1500 | 9 |
| Ammonium | y = 0.0011x – 0.0023 | R² = 0.9996 | 3 - 1500 | 9 |
| Potassium | y = 0.0021x + 0.0008 | R² = 0.9997 | 1 - 2500 | 9 |
| Magnesium | y = 0.0013x + 0.0323 | R² = 0.9996 | 3 - 1500 | 9 |
| Calcium | y = 0.0007x + 0.0055 | R² = 0.9983 | 3 - 1500 | 9 |
| Strontium | y = 0.0002x – 0.0007 | R² = 0.9987 | 10 - 2000 | 7 |

### 2.5 Limit of detection and limit of quantification

The limits of detection (LOD) and limits of quantification (LOQ) were calculated using the

185

*Orbital: Electron. J. Chem. 12 (4): 182-192, 2020*

curve parameters according to the expression: $LOD = 3,3 \, x \frac{s}{S}$ and $LOQ = 10 \, x \frac{s}{S}$, for LOD and LOQ respectively. Where, s is the linear coefficient of the equation and S is the slope of the analytical curve [37]–[39]. LOD were 0.5 µg L⁻¹ for $Li^+$ and 14.78 µg L⁻¹ for $SO_3^{2-}$ and LOQ were 1.50 µg L⁻¹ and 14.78 µg L⁻¹ for $Li^+$ and $SO_3^{2-}$, respectively (Table 2). Considering the sampling parameters,

with a total air volume of 1700 m³, the LOD of the anions ranged from 13 pg m⁻³ (methanesulfonate) to 114 pg m⁻³ ($SO_3^{2-}$), and the LOQ varied from 39 pg m⁻³ (methanesulfonate) at 342 pg m⁻³, ($SO_3^{2-}$). For cations, LOD ranged from 12 - 69 pg m⁻³ for $Li^+$ and $Ca^{2+}$, respectively, while LOQ ranged from 35 to 342 pg m⁻³ for $Li^+$ and $SO_3^{2-}$, respectively.

**Table 2.** Results for the sensitivity parameter of the proposed method.

| Species | µg L⁻¹ | | pg m⁻³ | | n |
|---|---|---|---|---|---|
| | LOD | LOQ | LOD | LOQ | |
| Fluoride | 0.94 | 2.82 | 22 | 65 | 9 |
| Lactate | 3.15 | 9.46 | 73 | 219 | 9 |
| Acetate | 1.21 | 3.62 | 28 | 84 | 9 |
| Propionate | 2.72 | 8.15 | 63 | 189 | 9 |
| Formate | 1.77 | 5.31 | 41 | 123 | 9 |
| Butyrate | 1.72 | 5.15 | 40 | 119 | 9 |
| Methanesulfonate | 0.56 | 1.69 | 13 | 39 | 9 |
| Pyruvate | 0.83 | 2.49 | 19 | 58 | 9 |
| Monochloroacetate | 2.11 | 6.34 | 49 | 147 | 9 |
| Bromate | 0.84 | 2.52 | 19 | 58 | 9 |
| Chloride | 1.67 | 5.01 | 39 | 116 | 9 |
| Nitrite | 2.21 | 6.63 | 51 | 154 | 9 |
| Trifluoroacetate | 1.31 | 3.92 | 30 | 91 | 9 |
| Bromide | 1.80 | 5.40 | 42 | 125 | 9 |
| Nitrate | 1.23 | 3.69 | 28 | 85 | 9 |
| Succinate | 0.98 | 2.95 | 23 | 68 | 9 |
| Sulfite | 4.93 | 14.8 | 114 | 342 | 7 |
| Sulfate | 4.84 | 14.5 | 112 | 336 | 9 |
| Oxalate | 0.74 | 2.21 | 17 | 51 | 9 |
| Tungstate | 1.90 | 5.70 | 44 | 132 | 9 |
| Molybdate | 0.88 | 2.63 | 20 | 61 | 9 |
| Phosphate | 2.11 | 6.33 | 49 | 146 | 9 |
| Chromate | 1.95 | 5.85 | 45 | 135 | 9 |
| Citrate | 1.92 | 5.77 | 45 | 134 | 9 |
| Lithium | 0.50 | 1.50 | 12 | 35 | 9 |
| Sodium | 0.70 | 2.10 | 16 | 49 | 9 |
| Ammonium | 0.75 | 2.25 | 17 | 52 | 9 |
| Potassium | 0.50 | 1.50 | 12 | 35 | 9 |
| Magnesium | 1.00 | 3.00 | 23 | 69 | 9 |
| Calcium | 3.00 | 9.00 | 69 | 208 | 9 |
| Strontium | 0.75 | 2.25 | 17 | 52 | 7 |

## 2.6 Precision and accuracy

Precision evaluations were determined using

the repeatability test is the correlation between the results of successive measurements of the same method, performed under the same instrument

186

*Orbital: Electron. J. Chem. 12 (4): 182-192, 2020*

conditions, analyst and location [39], [40]. The test was performed with standard solutions at concentrations of 100, 300 and 500 µg L$^{-1}$. The results were expressed in relative standard deviation (RSD%) and organized in two ways. The first was the intraday repeatability test (determination of the standard deviation with measurements taken on the same day) and the second test was the interday (determination of the relative standard deviation with measurements taken on different days).

Precision tests were conducted by recovery

tests, as certified reference materials for major ions in atmospheric PM are not commercially available. For complex samples, such as environmental samples, recovery values between 50% and 120% of the expected values are accepted [22]. Recovery ranged from 91% (strontium) to 105% (oxalate) for the concentration of 50 µg L$^{-1}$ of the added standard, from 90% (strontium) to 109% (phosphate) for additions of 100 µg L$^{-1}$ and 93 % (strontium) to 110% (phosphate) for additions of 300 µg L$^{-1}$. The recovery levels were within the accepted range, as shown in Table 3.

**Table 3.** Results of the precision and intraday and interday tests and recovery test.

| Species | Precision (RSD%) | | | | | | Recovery test (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Intraday (n = 10) | | | Interday (n = 5) | | | | | |
| | 100 | 300 | 500 | 100 | 300 | 500 | 50 | 100 | 300 |
| Fluoride | 0.36 | 0.38 | 0.06 | 0.51 | 0.47 | 0.08 | 90 | 107 | 95 |
| Lactate | 1.20 | 0.70 | 1.23 | 1.74 | 0.96 | 1.43 | 96 | 96 | 101 |
| Acetate | 0.39 | 1.62 | 0.73 | 0.52 | 1.94 | 0.95 | 104 | 104 | 98 |
| Propionate | 0.28 | 0.86 | 0.63 | 0.38 | 1.19 | 0.87 | 100 | 103 | 93 |
| Formate | 0.46 | 0.86 | 0.13 | 0.60 | 1.02 | 0.17 | 105 | 104 | 87 |
| Butyrate | 0.49 | 0.51 | 1.76 | 0.70 | 0.69 | 2.39 | 93 | 93 | 98 |
| Methanesulfonate | 1.01 | 0.64 | 1.86 | 1.37 | 0.89 | 2.48 | 96 | 100 | 97 |
| Pyruvate | 1.44 | 0.45 | 1.87 | 1.69 | 0.59 | 2.53 | 101 | 96 | 95 |
| Monochloroacetate | 0.25 | 0.72 | 0.03 | 0.34 | 0.85 | 0.03 | 94 | 101 | 93 |
| Bromate | 0.85 | 0.64 | 0.32 | 1.08 | 0.78 | 0.46 | 97 | 96 | 94 |
| Chloride | 2.29 | 1.12 | 0.57 | 3.17 | 1.36 | 0.66 | 99 | 100 | 99 |
| Nitrite | 0.78 | 0.85 | 0.15 | 1.19 | 0.99 | 0.21 | 96 | 102 | 103 |
| Trifluoroacetate | 1.90 | 0.27 | 0.55 | 2.52 | 0.39 | 0.66 | 97 | 104 | 96 |
| Bromide | 1.98 | 2.14 | 0.12 | 2.71 | 2.95 | 0.18 | 100 | 100 | 90 |
| Nitrate | 1.72 | 2.18 | 0.21 | 2.47 | 3.00 | 0.28 | 96 | 98 | 100 |
| Succinate | 0.28 | 0.80 | 0.28 | 0.38 | 1.02 | 0.34 | 98 | 99 | 105 |
| Sulfite | 0.31 | 2.01 | 1.03 | 2.14 | 1.08 | 0.38 | 98 | 100 | 99 |
| Sulfate | 2.60 | 0.26 | 0.35 | 3.03 | 0.36 | 0.41 | 91 | 101 | 97 |
| Oxalate | 0.41 | 0.35 | 0.03 | 0.49 | 0.51 | 0.03 | 105 | 101 | 103 |
| Tungstate | 1.85 | 1.52 | 1.59 | 2.68 | 1.87 | 1.87 | 94 | 87 | 96 |
| Molybdate | 0.23 | 0.73 | 0.68 | 0.33 | 0.96 | 0.83 | 98 | 101 | 92 |
| Phosphate | 1.02 | 1.26 | 0.43 | 1.43 | 1.49 | 0.54 | 100 | 109 | 110 |
| Chromate | 3.28 | 0.82 | 0.90 | 4.40 | 1.17 | 1.25 | 89 | 91 | 92 |
| Citrate | 1.51 | 0.72 | 0.58 | 1.95 | 0.99 | 0.76 | 104 | 102 | 96 |
| Lithium | 0.35 | 0.09 | 0.20 | 0.46 | 0.13 | 0.32 | 101 | 100 | 100 |
| Sodium | 3.58 | 3.92 | 1.53 | 16.80 | 6.17 | 1.88 | 100 | 99 | 99 |
| Ammonium | 0.17 | 0.47 | 0.13 | 0.30 | 0.76 | 0.18 | 98 | 97 | 98 |
| Potassium | 3.62 | 1.33 | 0.38 | 5.20 | 1.90 | 0.60 | 100 | 101 | 99 |
| Magnesium | 6.14 | 2.42 | 1.27 | 8.95 | 3.37 | 1.83 | 99 | 98 | 99 |
| Calcium | 8.48 | 0.59 | 1.41 | 11.70 | 0.81 | 2.10 | 96 | 98 | 97 |
| Strontium | 8.03 | 1.76 | 1.66 | 11.50 | 2.63 | 2.53 | 91 | 90 | 93 |

Accuracy tests intraday and interday for repeatability expressed as RSD% in three concentration ranges 100, 300 and 500 µg L$^{-1}$ and recovery test performed with the addition of a standard to the PM sample in three concentration ranges 50, 100 and 300 µg of L$^{-1}$.

187

*Orbital: Electron. J. Chem. 12 (4): 182-192, 2020*

## 2.7 Ruggedness

According to IUPAC, the robustness of the method is the ability of the results obtained to remain unchanged under low variations in the studied parameters [35]. In this study, robustness was assessed by analysis samples in different conditions, such as: (i) variation of column temperature (variation between 35 and 38 °C), (ii) flow variation (variation between 0.35 and 0.38 mL min$^{-1}$) and (iii) injection volume variation (variation between 500 and 1500 µL) [41], [42].

As shown in Table 4, the effects in the peak areas were observed and remained in constant amplitude in the levels of variation of the limits of accuracy, precision and selectivity. Moreover, the studied variations resulted in very small variations in the method's behavior, and are therefore despised.

**Table 4.** Variation of detector response (µS) by changing some parameters of the method.

|  | Variation in detector response (µS) | | | |
|---|---|---|---|---|
|  | **Column temp.** | **Flow variation** | **Injection volume** | **RSD%** |
| Fluoride | 1.1142 | 1.1184 | 1.1076 | 0.49 |
| Lactate | 0.1539 | 0.1553 | 0.1537 | 0.57 |
| Acetate | 0.2376 | 0.2421 | 0.2324 | 2.05 |
| Propionate | 0.1836 | 0.1866 | 0.1823 | 1.20 |
| Formate | 0.3922 | 0.3946 | 0.3895 | 0.65 |
| Butyrate | 0.1464 | 0.1458 | 0.1454 | 0.33 |
| Methanesulfonate | 0.1681 | 0.1691 | 0.1664 | 0.81 |
| Pyruvate | 0.1392 | 0.1394 | 0.1388 | 0.22 |
| Monochloroacetate | 0.1664 | 0.1673 | 0.1653 | 0.60 |
| Bromate | 0.1173 | 0.1178 | 0.1162 | 0.69 |
| Chloride | 0.5249 | 0.5282 | 0.5196 | 0.83 |
| Nitrite | 0.3945 | 0.3974 | 0.3914 | 0.76 |
| Trifluoroacetate | 0.1002 | 0.1003 | 0.0996 | 0.37 |
| Bromide | 0.1902 | 0.1894 | 0.1868 | 0.93 |
| Nitrate | 0.2287 | 0.2274 | 0.2254 | 0.72 |
| Succinate | 0.1402 | 0.1409 | 0.1397 | 0.43 |
| Sulfite | 0.2984 | 0.2981 | 0.2979 | 0.08 |
| Sulfate | 0.2985 | 0.2978 | 0.2983 | 0.12 |
| Oxalate | 0.2993 | 0.3011 | 0.2974 | 0.62 |
| Tungstate | 0.0642 | 0.0651 | 0.0637 | 1.11 |
| Molybdate | 0.1367 | 0.1364 | 0.1374 | 0.38 |
| Phosphate | 0.1135 | 0.1152 | 0.1117 | 1.54 |
| Chromate | 0.0943 | 0.0942 | 0.0947 | 0.29 |
| Citrate | 0.1007 | 0.1018 | 0.0994 | 1.19 |
| Lithium | 1.6523 | 1.6491 | 1.6492 | 0.11 |
| Sodium | 0.6431 | 0.6605 | 0.6542 | 1.35 |
| Ammonium | 0.5447 | 0.5376 | 0.5436 | 0.71 |
| Potassium | 1.0501 | 1.0988 | 1.0784 | 2.27 |
| Magnesium | 0.7355 | 0.7521 | 0.7311 | 1.50 |
| Calcium | 0.3544 | 0.3577 | 0.3556 | 0.47 |
| Strontium | 0.1367 | 0.1351 | 0.1312 | 2.11 |

## 2.8 Test for matrix sample effect

The matrix effect is defined as a change in analytical signal caused by an interference found in the sample. This effect was evaluated by comparing the slope (a) of two linear regression curves, acquired with and without standard addition [43], [44]. The first curve was made from eight different levels of ion concentration added to the actual sample of particulate material (standard + sample), while the second curve was a standard aqueous ion solution (standard) at eight different concentration levels, ranging from 1 to 500 µg L$^{-1}$

188

*Orbital: Electron. J. Chem. 12 (4): 182-192, 2020*

[22], [45]. Thus, the evaluation was performed by comparing the slopes of the two curves (standard + sample / standard). When the slopes of both curves are the same or very close, it tends to approach 1, meaning that there is no matrix effect acting on the analysis. Thus, the method developed in this study is not susceptible to the matrix effect, as the results ranged from 1.1 for $SO_4^{2-}$ to 1.0 for $Br^-$. Moreover, there is no need to use the standard addition method (which is time consuming) for the quantification of ions in PM samples, which would consequently decrease the analytical frequency among other factors.

## 2.9 Test with real samples

The method was tested by analyzing five (5) samples of atmospheric PM of fractions of size PM 2.5 µm and PM 10 µm collected at the Naval Base Station of Aratu, according to the optimized conditions. The chromatograms of one of the samples are shown in Figure 2, where 11 anions (Fig 2a) and 6 cations were detected by the method developed (Fig 2b). The average conditions obtained can be found in Table 5.
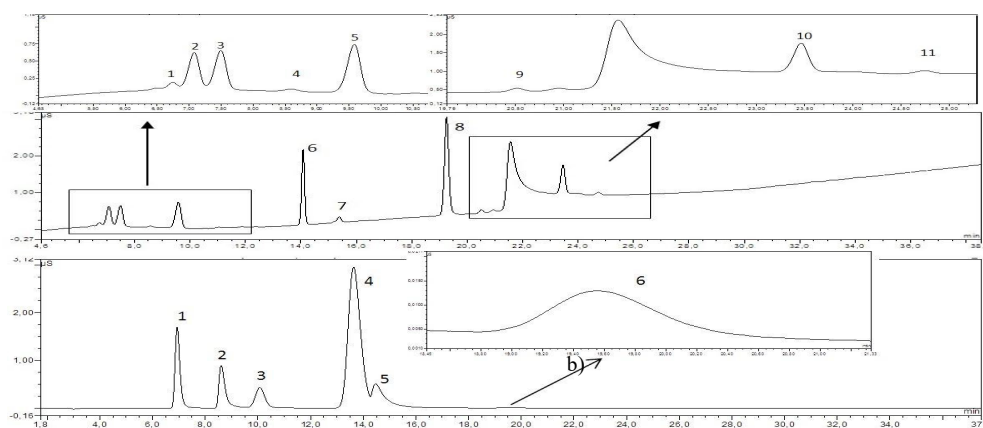


**Figure 2** Chromatograms of a real sample of PM, (a) anions 1- Fluoride (0.13 ng m⁻³), 2-Lactate (5.00 ng m⁻³), 3-Acetate (3.86 ng m⁻³), 4- Formate (3.17 ng m⁻³), 5- Pyruvate (0.14 ng m⁻³), 6- Chloride (3.39 ng m⁻³), 7- Nitrite (0.68 ng m⁻³) 8- Nitrate (14.82 ng m⁻³), 9- Succinate (0.51 ng m⁻³) -3), 10- Sulphate (3.35 ng m⁻³), 11- Oxalate (0.44 ng m⁻³); (b) 1- Sodium (7.19 ng m⁻³), 2- Ammonium (5.59 ng m⁻³), 3- Potassium (2.20 ng m⁻³), 4- Magnesium (28.26 ng m⁻³), 5- Calcium (9.62 ng m⁻³), 6- Strontium (0.97 ng m⁻³).

**Table 5**. Average concentrations of real fraction samples of size PM 2.5 and PM 10 (ng m⁻³).

| Species | (Mean ± SD) | |
|---|---|---|
| | **PM$_{2,5}$** | **PM$_{10}$** |
| Fluoride | 0.40 ± 0.14 | 1.01 ± 0.13 |
| Lactate | 14.69 ± 3.32 | 28.35 ± 3.94 |
| Acetate | 11.12 ± 2.04 | 24.19 ± 1.72 |
| Formate | 11.06 ± 1.73 | 22.77 ± 3.13 |
| Pyruvate | 0.25 ± 0.06 | 0.66 ± 0.33 |
| Chloride | 42.59 ± 19.07 | 60.38 ± 13.27 |
| Nitrite | 5.74 ± 2.99 | 10.56 ± 5.59 |
| Nitrate | 32.45 ± 12.26 | 57.99 ± 12.01 |
| Succinate | 1.42 ± 0.50 | 3.60 ± 0.55 |
| Sulphate | 46.7 ± 14.78 | 49.5 ± 15.32 |
| Oxalate | 2.27 ± 0.94 | 5.32 ± 0.36 |
| Sodium | 45.42 ± 16.46 | 69.10 ± 14.18 |
| Ammonium | 19.61 ± 4.81 | 37.76 ± 6.13 |
| Potassium | 9.71 ± 4.33 | 17.88 ± 4.93 |
| Magnesium | 48.7 ± 22.45 | 84.5 ± 36.54 |
| Calcium | 35.25 ± 11.42 | 94.01 ± 24.53 |
| Strontium | 2.52 ± 0.66 | 6.56 ± 1.26 |

The analytes were identified by comparing the retention times of the analytical standards used in the development of the method with those found in the real PM samples. Quantification was performed in triplicate, using a standard calibration curve. In the studied samples, butyrate, methanesulfonate, monochloroacetate, bromate, trifluoroacetate, bromide, sulfite, tungstate, molybdate, phosphate, chromate, citrate and lithium ions were not found above LOD, however, the other ions were detected.

The analyzed samples showed that the PM is of primary origin, this can be proved by the diagnostic reasons formate / acetate, which presented values lower than one unit, this statement can be proved by the ratios $NH_4^+$ / $SO_4^2$, which also showed values less than 1, these numbers indicate that the conversion of gas to particle was not a significant source of PM 2.5

189

*Orbital: Electron. J. Chem. 12 (4): 182-192, 2020*

for the atmosphere. Moreover, the abundance of chloride, nitrate, sodium, ammonium, magnesium and calcium, which are corresponding to 74% and 71% in PM 10 and PM 2.5 fractions, respectively, show a strong contribution from the sea spray and / or resuspending of crustal material.

## 3. Material and Methods

### 3.1 Reagents, solutions, and analytical standards

The standard solutions and eluents used during the experiments were prepared with ultrapure water of resistivity greater than 18,2 MΩ cm at 25 °C and conductivity 0,054 µS cm$^{-1}$ at 25ºC, obtained by the Milli-Q purification system (Millipore Corporation, U.S.A.). The stock solutions were prepared from the sodium, chloride, sulfate, and ammonium salts of the analytes studied with ACS grade or equivalent (Merck e J. T. Baker, USA) to the initial concentration of 1000 mg L$^{-1}$.

The solutions were stored at -18ºC for up to 1 month. The analytical solutions were prepared by successive dilutions from the stock solution. For quantification, the external standardization method was used with nine levels of concentration: 1, 3, 7, 10, 30, 50, 100, 300, and 500 µg L$^{-1}$. In this study, ultrapure water was used for the internal eluent generation system (EluGen™ EGC III KOH, Dionex™, USA) for the ACS grade (Merck – U.S.A.) anions and sulfuric acid system at 25,0 mmol L$^{-1}$ for the cation system.

### 3.1 Atmospheric sample collection and sample preparation

Samples of PM 2.5 and PM 10 (*n* = 3 for each fraction of size, at sea level) were collected at the Naval Base Station of Aratu and in the Bay of Todos os Santos located near the capital Salvador, in Bahia, Brazil. Both PM 2.5 and PM 10 samples were collected by using two Hi-Vol sampler PM 2.5 and PM 10 (Energetica - Brazil) equipped with a quartz filter and PTFE filter (254 x 203 mm and 0.25 µm pore size, Sartorius, Germany). Sampling time was 24 h under a flow rate of 1.3 m$^3$ min$^{-1}$. 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 ºC) prior to analysis to prevent the evaporation of volatile components. These were the samples used in this study for validation of our analytical methodology.

As PM samples were extracted by adding 1 mL of a 2% (v / v) solution of ultrapure water (Millipore purification system - Millipore Corporation, USA - with resistance greater than 18.2 M, 2 cm$^{-1}$ and conductivity 0.054 µS cm$^{-1}$ at 25 ° C) and isopropanol (Analytical grade JT Baker) on the fractions of the filters in the falcon tubes. Then, the tubes were brought to mechanical agitation for 10 min. on a Vortex-type stirrer - 3800 RPM. The extracts were filtered with disposable filters for IC Millex syringe (Millipore - USA) with hydrophilic modified PTFE membrane, of 0.22 µm pore coupled with disposable syringes and transferred to injection vials.

### 3.2 Analytical instrumentation and analysis

For the development of the method, a IC - conductivity detector with double channel, model HPIC-Aquion and HPIC-Integrion, was used for cations and anions, respectively, with automatic injector model Dionex AS-DV 40 and regeneration of system eluents (both from Thermo, USA).

Anion and cations were determined using analytic columns IonPac AS19 (2 × 250 mm) and IonPac AG12A (2 × 250 mm) with its guard columns IonPac AG19 (2 × 50 mm) and IonPac CG12A (2 × 50 mm), respectively. The chromatographic system used self-suppressors SRS (Self Regenerating Suppressor), model CERS-500 (2 mm film thickness, Dionex, USA), and AERS-500 (2 mm film thickness, Dionex, USA), using suppression current of 74 and 38 mA, for cations and anions respectively.

## 4. Conclusions

In this study, a new method was developed and validated for the determination of 31 water-soluble ions in environmental samples by ion chromatography simultaneously for cations and anions with conductivity detector. The number of analytes used in this study represents a significant advance in the chromatographic methods frequently reported in the literature, mainly because they present good equipment stability, with a total analysis time of 37 minutes per

190

*Orbital: Electron. J. Chem. 12 (4): 182-192, 2020*

sample.

The proposed method was validated in accordance with international rules and all analytical parameters proved to be adequate for the analysis of environmental samples. The method was applied by analyzing real samples of atmospheric PM samples with 10 µm and 2.5 µm, aerodynamic diameter collected at Aratu Naval Base Station and in Todos os Santos Bay, in Bahia, Brazil. It was possible to determine 17 ionic species such as mono, di and tricarboxylic acids, chromate, molybdate and vanadate, strontium and elements of crustal origin, important in the study of environmental relations resulting from anthropic and biogenic activities. Therefore, this method can be used to analyze samples of atmospheric PM and in other matrices such as gas phase, rainwater and river and soil, in addition to geochemistry, oceanography and glaciology, as a useful tool for mass balance calculations of several substances, as well as in the speciation of sulfur compounds, nitrogen and organic acids found in various environmental samples.

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191

*Orbital: Electron. J. Chem. 12 (4): 182-192, 2020*

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192

*Orbital: Electron. J. Chem. 12 (4): 182-192, 2020*