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DOI 10.1007/s00769-011-0844-4

PRACTITIONER’S REPORT

Uncertainty estimation of anions and cations measured by ion chromatography in fine urban ambient particles ($PM_{2.5}$)

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Received: 23 June 2011 / Accepted: 12 October 2011

Abstract The present work presents a measurement uncertainty evaluation according to Guide to the Expression of Uncertainty in Measurement (GUM) of the concentration of the cations K^+ and Li^+ and anions NO_3^{-2} and SO_4^{-2} in fine airborne particulate matter, refers to particles less than 2.5 μm in diameter ($PM_{2.5}$), as measured by ion chromatography (US-EPA 300 method). The GUM method is not typically used to report uncertainty. In general, the analytical results only report the measurement’s standard deviation under repetition as an uncertainty; thus, not all sources of uncertainty are considered. In this work, the major sources of uncertainty regarding the measurements were identified as contributions to linear least square regression lines, repeatability, precision, and trueness. The expanded uncertainty was approximately 20% for anions and cations. The largest contribution to uncertainty was found to be repeatability.

Keywords Uncertainty estimation · Air quality · Anions · Cations · PM2.5 · Ambient particles · GUM

Introduction

Urban ambient fine particles, smaller than 2.5 μm ($PM_{2.5}$), are characterized by their physical attributes and their chemical composition, which can influence their effect on human health [1–4]. The ionic composition of ambient particles can be useful in identifying their atmospheric source [5–9]. For example, calcium carbonate ($CaCO_3$) and calcium nitrate ($CaNO_3$) are usually found in arid regions because of the suspension of soils [10, 11], whereas ammonium sulfate ($(NH_4)_2SO_4$) and ammonium nitrate (NH_4NO_3) are commonly found in air masses influenced by anthropogenic emissions [12–14].

Many important environmental decisions are based on the results of chemical quantitative analysis. It is thus important to verify the quality of such results. Uncertainty is a useful way to establish the quality of a measurement and determine whether or not the results are sufficient for the purpose of the study [15]. The uncertainty can be defined as “a parameter associated with the result of a measurement that characterizes the dispersion of values reasonably attributed to the measurement” [16].

The concept of uncertainty is widely recognized among analytical chemists. Replicate preparation and testing of samples generates a range of results. This intrinsic variability of results represents the analytical measurement uncertainty. In principle, when estimating analytical measurement uncertainty, all significant components of uncertainty must be identified and quantified [17–19]. Components that affect the analytical measurement uncertainty include sampling, handling, transport, storage, preparation, and testing. Components of uncertainty that do not contribute significantly to the total uncertainty of the test result can be neglected. The measurement of uncertainty seems quite simple but many steps can be difficult to identify or quantify and can be time consuming [20].

A unique protocol does not exist for analytical measurement uncertainty estimation [16, 21–26]. One of the most detailed and popular techniques is the ISO Guide to

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the Expression of Uncertainty in Measurement (GUM), which was first published in 1993. This guide establishes general rules to evaluate and express uncertainty for quantitative analytical measurements [22, 26, 27]. Many other schemes have been proposed some with more emphasis on routine data or statistical approaches [19, 24, 28].

The evaluation of uncertainty requires the analyst to closely evaluate all possible sources of uncertainty. However, although a detailed study of this kind may require a considerable effort, it is essential for the effort to not be disproportionate (i.e., concentrating the effort on the largest contribution can provide a good uncertainty estimation). For routine quality assurance, a detailed identification and quantification of all the uncertainty sources could be useful to focus quality control on those steps that readily demonstrate a higher contribution to the total uncertainty of the measurement. Generally, such identification and quantification can be a documented contribution to differentiated quality control for different analytical procedures [15].

The aim of this study was to develop a complete estimation of uncertainty for the determination of anions and cations in urban particles using a MetONE Super SASS, as sampling device, ionic chromatography as the analytical quantification technique, and the GUM approach for uncertainty calculation. On this basis, we demonstrated that the calculated uncertainties were different for each measurement (ions) and focused on minimizing the effect of the main uncertainty sources on the total uncertainty.

Materials and methods

Chemicals and reagent preparation

All chemicals were of high purity (99.5%, Merck). Solutions were prepared in clean and dry glassware. Solutions were prepared using the volumetric method. Volumes ranging from 30 to 200 µL were measured with a P100 micropipette (Gilson) or class A volumetric flasks. The stock standard solutions of Nitrate, Sulfate, Lithium, and Potassium at (1000 ± 2) mg L^{-1} nominal ion concentration were certified commercial solutions (CertiPur, Merck).

Dionex commercial eluent for anions and cations was used; the eluent contained 30 mmol L^{-1} potassium hydroxide (KOH) and 20 mmol L^{-1} methanesulfonic acid (CH_4O_3S).

Sample collection

The sampling was performed using a Met One Super SASS air sampler [29] placed on the roof of the Chemistry Laboratory of the National Center for Environment (Centro Nacional del Medio Ambiente CENMA), which is located in the City of Santiago, Chile. Particle samples were collected on 46.2 mm PPE filters (Whatman). Air sampling was performed at a flow rate of 6.9 $m^3\ h^{-1}$ for 48-h periods from January 4 to 6, 2010. The Met One Super SASS was specifically designed to collect $PM_{2.5}$ particulate samples for further analysis of chemical species. The instrument has an 8-channel sampler with multiple-event capability. Samples were collected in each of the 8 channels simultaneously (i.e., 8 filters were collecting during the same period of time and under identical meteorological conditions). Prior to sampling, the filters for both of the instruments were conditioned for 24 h and then weighed in a controlled environment chamber maintained at a relative humidity of (35 ± 2) % and a temperature of (22 ± 2) °C. Upon reception, samples are stored in sealed containers, and refrigeration will minimize these losses.

Exposed filters were typically weighed within a day or two of collection, which involved returning the filters to the controlled environment chamber, conditioning the filters for 24 h, and then weighing the filters to determine sample weight.

Extraction of water-soluble anions and cations

The 8 collected aerosol filters were ultrasonically extracted for 15 min into 0.5 L of deionized distilled water (18 MΩ, MilliQ system, Millipore). The extracted solution was then filtered in portions through a syringe PPE filter pore size 0.25 µm (Orange Scientific). Samples were then introduced into the ion chromatograph to measure the charged species.

Analysis using ion chromatography

The concentration of nitrate and sulfate anions (NO_3^- and SO_4^-) and Lithium and Potassium cations (Li^+ and K^+) was determined with a Dionex ICS-3000 dual system consisting of a dual pump (DP) module, an eluent generator (EG) module, a detector chromatography (DC) module (single temperature zone configuration), and an autosampler (AS) (Table 1). The ionic species were identified and quantified by interpolation on a proper calibration curve. All experiments were performed at room temperature and lasted approximately 12 min for each injected sample.

Preparation of calibration standards and quality control standards

The calibration standard solutions were prepared through successive additions of the principal standard solution to

Table 1 Instrumental conditions of anions and cations concentration measurement using ion chromatography

Instrument	Dionex ICS-3000 dual system
Eluent generator	Dionex ICS-3000 eluent generator (EG) with dual channel EluGen Cartridges
Guard column	IonPack AG11-HC Dionex (anions)
	IonPack CG12 Dionex (cations)
Column	IonPack AS11-HC Dionex (anions)
	IonPack CS12 Dionex (cations)
Mobile phase—eluent	30 mmol L^{-1} KOH (anions) and 20 mmol L^{-1} CH_4O_3S (cations)
Eluent flow	1.00 mL min^{-1}
Sample volume	25 µL
Injection technique	Direct auto-sampling device model AS-DV
Detection	Conductivity detector (CD) with integrated cell held at 35 °C
Conductivity Suppressor	ASRS 300 4-mm
	CSRS 300 4-mm
Data analysis software	Chromeleon v2.0

deionized water (18.2 MΩ cm, Milli-Q System, Millipore) for each ion (Fig. 1). The range for the calibration curves of all ions under study was from 0.20 mg L^{-1} to 10 mg L^{-1}. The main stock solution was prepared from certified commercial solutions of (1000 ± 2) mg L^{-1} nominal ion concentration (CertiPur, Merck). All prepared solutions were stored in a refrigerator at (4 ± 2) °C. Calibration curves were constructed by plotting peak areas for each ion against the concentration. The quality requirement for the acceptance of the calibration function was established as a correlation coefficient of $r^2 \geq 0.995$.

Experimental design and uncertainty estimation procedure

The procedure used to evaluate the uncertainty associated with the determination of the ion concentration by IC can be divided into the following steps [26]:

1. Description of the measurement procedures
2. Specification of the measurand and relationship between the measurand and the variables
3. Identification of uncertainty sources
4. Effect diagram and quantification of individual uncertainties
5. Calculation of the combined uncertainty
6. Expanded uncertainty
7. Expression of results

Step 1: Description of the measurement procedures. Figure 2 shows the flowchart for the measurement procedures. The flowchart diagram shows the main analytical process used for the sampling process up to obtaining the results in this work. Each box represents the main analytical process used to obtain results.

Step 2: Specification of the measurand and relationship between the measurand and the variables. The following

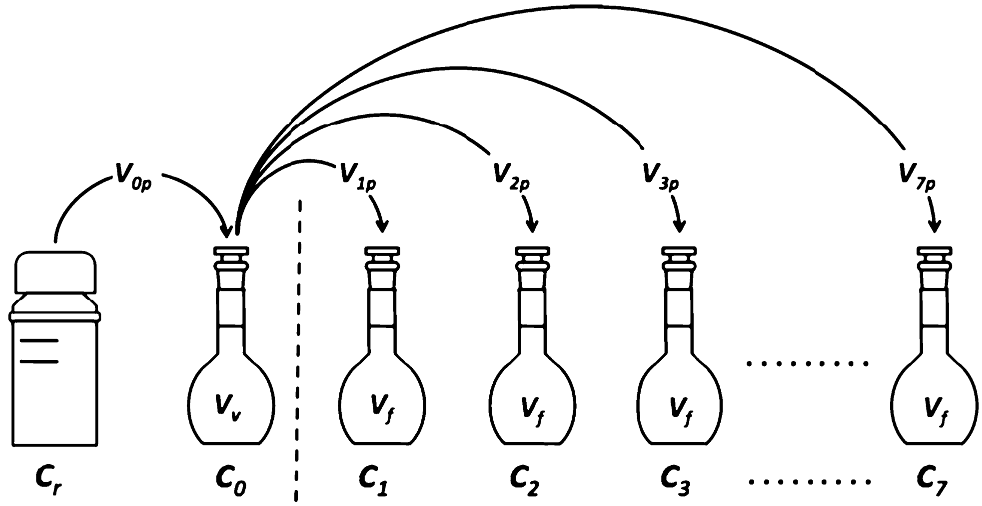

Fig. 1 Diagram for calibration curve standard preparation

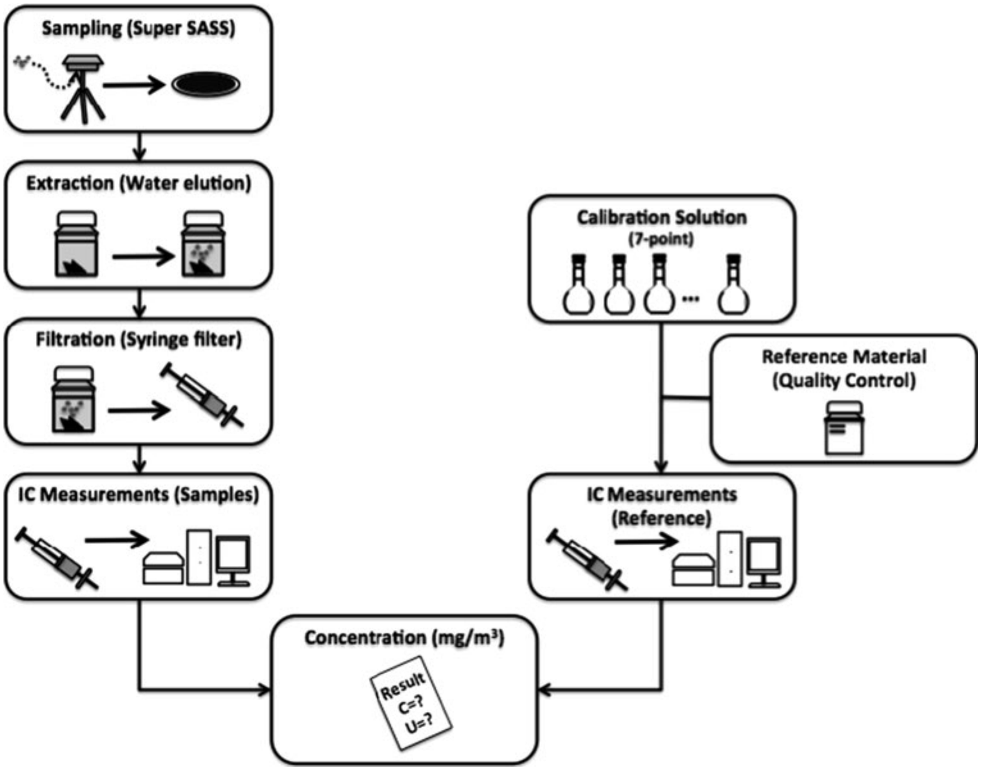

Fig. 2 Flowchart of the main analytical process

mathematical model can express the atmospheric concentration of ions in particulate matter:

$$c_i = c_d^a f_c \tag{1}$$

where c_i is the atmospheric concentration of ions in the particular matter (mg m^{-3}) (Eq. 1). c_d^a is the concentration determined (mg $^{-1}$) by the calibration curve using the peak area from chromatogram A (μS min); b is the slope of the calibration curve (μS min L mg^{-1}) (Eq. 2); and f_c is a conversion factor for the ion concentration in the solution with respect to that in the air and depends on the air volume sampled (V_s in m^3) and the volume of the extraction (V_e in L) (Eq. 3). In addition, f_p is the reproducibility factor and f_r is the instrumental recovery factor.

$$c_d^a = \frac{A}{b} f_r f_p \tag{2}$$

$$f_c = \frac{V_e}{V_s} \tag{3}$$

Steps 3 and 4: Identification of uncertainty sources, building cause and effect diagrams and quantification of individual uncertainties. According to Eq. 1, the cause and effect diagram can be drawn from the sources of uncertainty for this method (Fig. 3).

Extracting volume (V_e). The uncertainty in volumetric operations is associated with the following sources: the uncertainty of the volumetric flask or pipette calibration, the temperature uncertainty resulting from the use of glassware at a temperature different from that used in calibration, and the repeatability of the volumetric measurement.

The data provided by the manufacturers for tolerances (O) of the flasks or pipettes, which represent an extreme value of the possible error expressed by the specifications of a measuring instrument, were used as estimates of the calibration uncertainty. The distribution was reported by a rectangular distribution [30]. Thus, the uncertainty associated with calibration can be expressed according to:

$$u(V_o) = \frac{O}{\sqrt{3}} \tag{4}$$

The uncertainty linked with the temperature (T) can be calculated from the estimation of the temperature range and the volume expansion coefficient of water. The standard uncertainty caused by the temperature assuming a triangular distribution is as follows:

$$u(V_T) = \frac{\gamma V_n \Delta T}{\sqrt{3}} \tag{5}$$

where γ is the volume expansion coefficient for water and corresponds to 2.1×10^{-4} °C^{-1} [16]. V_n is the nominal volume and ΔT corresponds to the difference between the room temperature and the calibration temperature.

The uncertainty resulting from variations in filling can be estimated from a repeatability study. A series of ten fill and weigh experiments were designed using flasks and

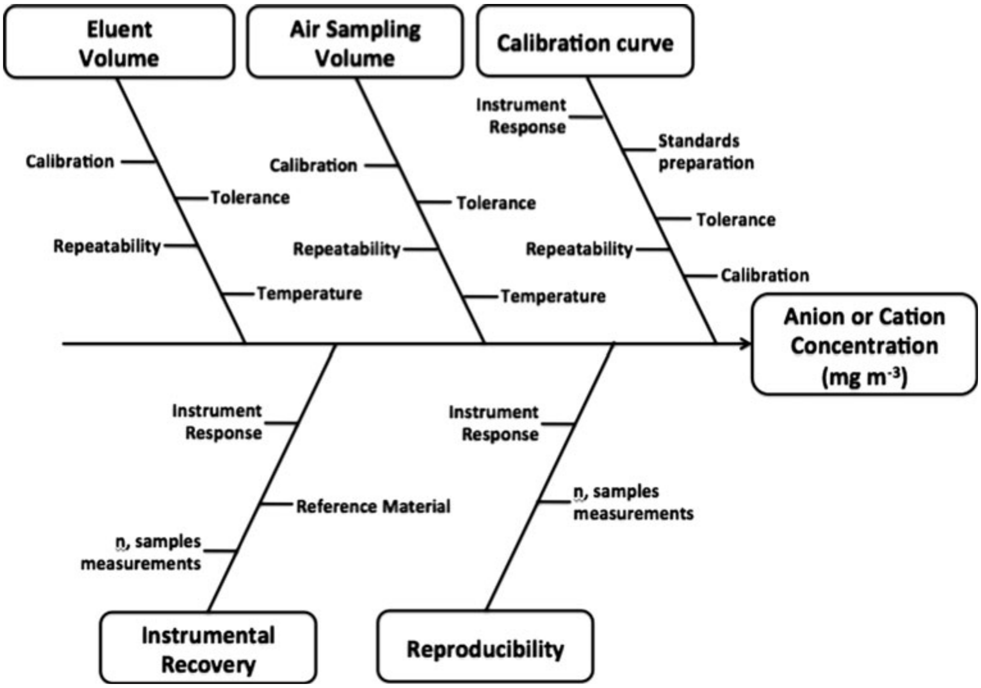

Fig. 3 Cause–effect diagram for the main sources of uncertainty

pipettes for a standard deviation. This series could then be used directly as a standard uncertainty (a normal distribution is assumed). The reproducibility can be estimated according to:

$$u(V_p) = \frac{s}{\sqrt{n}} \tag{6}$$

where s is the standard deviation expressed in volume units of the n measurements employed with the volumetric material.

In the end, the uncertainty of the volumetric uncertainty is the result of the uncertainty from the combination of variables expressed in Eq. 4, 5, and 6:

$$uV = \sqrt{u(V_o)^2 + u(V_T)^2 + u(V_p)^2} \tag{7}$$

associated with the mathematical calculation of the airflow volume was considered:

$$V_a = V_f \frac{P_s T_a}{T_s P_a} t_s f_p f_o \tag{8}$$

where V_a is the air sampling volume (L); V_f is the flow volume of the sampling instrument (L min^{-1}); P_s is the standard pressure (101330 Pa); P_a is the sampling pressure (Pa); T_s is a standard temperature (25 °C); T_a is the ambient temperature (°C); t_s is the sampling time (min); f'_p is the flow reproducibility factor and is calculated in the same way as Eq. 4 and f'_o is the flow tolerance factor and is also calculated according to Eq. 4. The Super SASS should display a flow within ±4% of 6.7 L min^{-1} [29]. The uncertainty in the air sampling volume can therefore be expressed as follows.

$$u(V_a) = V_a \sqrt{\left(\frac{u(V_f)^2}{V_f}\right) + \left(\frac{u(T_a)}{T_a}\right)^2 + \left(\frac{u(P_a)}{P_a}\right)^2 + \left(\frac{u(t_s)}{t_s}\right)^2 + \left(\frac{u(f'_p)}{f'_p}\right)^2 + \left(\frac{u(f'_o)}{f'_o}\right)^2} \tag{9}$$

Air sampling volume (V_a). The air sampling volume uncertainty can arise from the calibration uncertainty of the airflow, the reproducibility of the air sampling volume in each channel of the sampling equipment, the temperature, and the pressure. The rigorous identification of the air sampling volume uncertainty is outside the scope of this paper, so only the main uncertainty contribution

Calibration curve. The linear regression model shown in Eq. 10 is applied for calibration.

$$A_j = bc_j \tag{10}$$

where the predicted content c_j is calculated from A_j of a peak area in the chromatogram. The regression coefficient, b, is estimated from the calibration data set $\{c_j, A_j\}$ according to:

$$b = \frac{\sum_{j=1}^{n} c_j A_j}{\sum_{j=1}^{n} c_j^2} \tag{11}$$

The following equation is used to calculate the standard measurement uncertainty of the content of a sample (c_d):

$$u(c_d, A_d) = \frac{s_r^2}{b}\sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(c_d - \bar{c})^2}{\sum_{j=1}^{n} (c_j - \bar{c})^2}} \tag{12}$$

where s_r is a residual standard deviation calculated according to Eq. 13; n is the total number of data points used for the calculation; p is the number of measurements made to determine a particular value; $\bar{c}$ is the mean concentration value of the different stock standard solutions; and c_j is the concentration for each calibration standard observed at each calibration point as calculated by volumetric preparation.

$$s = \sqrt{\frac{\sum (A_j - (bc_j))^2}{n - 2}} \tag{13}$$

A rigorous explanation of the uncertainty calculation of the calibration curve is outside the scope of this paper.

The main stock solution was prepared from certified commercial solutions according to Eq. 14

$$c_0 = c_r \frac{V_{0p}}{V_v} \tag{14}$$

where c_0 is the concentration of the ion stock solution (mg mL^{-1}); c_r is the concentration of the ion certified reference material (mg mL^{-1}); V_{0p} is the pipette volume in the ion certified reference material (mL); and V_v is the end volume of 50 mL volumetric flask. After that, seven working solutions were prepared with concentrations from 0.20 to 10.0 mg/L, according to Eq. 15.

$$c_i = c_0 \frac{V_{ip}}{V_f} \tag{15}$$

where c_i is the concentration of the i-esima working solutions (mg mL^{-1}); V_{ip} is the pipette volume in the ion stock solution (mL); and V_f is the end volume of 50 mL volumetric flask. The uncertainties of the working calibration solution concentrations for the curves were associated with the uncertainty of the working reference solution concentrations. The pipette and volumetric flask volumes for the preparation of the working solutions can be calculated according to:

$$u(c_k) = c_k \sqrt{\left(\frac{u(c_r)}{c_r}\right)^2 + \left(\frac{u(V_p)}{V_p}\right)^2 + \left(\frac{u(V_v)}{V_v}\right)^2} \tag{16}$$

Reproducibility. The uncertainty resulting from variations in the concentration can be estimated with a reproducibility study [31]. A series of independent samples were measured in the ionic chromatograph to obtain the standard deviation, which can then be used directly as standard uncertainty (a normal distribution is assumed). The reproducibility can be estimated according to Eq. 6.

Instrumental recovery. The instrumental recovery factor is the only input quantity that takes the sample preparation of the calibration curve into account [32, 33]. The recovery method is calculated according to:

$$f_{rec} = \frac{\bar{C}_{\text{obs}}}{C_M} \tag{17}$$

The uncertainty associated with recovery ($u(f_r)$) is then estimated as follows:

$$u(f_r) = f_r \sqrt{\left(\frac{s_o^2}{n\bar{c}_o^2}\right) + \left(\frac{u(c_M)}{c_M}\right)^2} \tag{18}$$

where s_o is the standard deviation of the n measurement of the reference material; $\bar{c}_o$ is the average of the measurement; c_M is the reference concentration; and $u(c_M)$ is the uncertainty of the reference value.

Steps 5, 6, and 7: Combined uncertainty calculation, expanded uncertainty, and expression of results. The combined standard uncertainty for the atmospheric concentration of ions in PM$_{2.5}$ (calculated according to the model above using Eq. 1) can be determined using:

$$u(c_i) = c_i \sqrt{\left(\frac{u(c_d)}{c_d}\right)^2 + \left(\frac{u(V_a)}{V_a}\right)^2 + \left(\frac{u(V_e)}{V_e}\right)^2 + \left(\frac{u(f_r)}{f_r}\right)^2 + \left(\frac{u(f_p)}{f_p}\right)^2}. \tag{19}$$

The result should be stated together with the expanded uncertainty, *U*, which is calculated using a coverage factor of $k = 2$. This operation provides a level of confidence of approximately 95% according to:

$$U(c_i) = k\,u(c_i) \tag{20}$$

The result from of the preceding operations is recommended to be expressed as $c_i \pm U(c_i)$.

UncertaintyMANAGER®: Uncertainty estimation software. UncertaintyMANAGER® software was used for the evaluation of measurement uncertainty in this work [34]. The software implements the Eurachem/CITAC guide “Quantifying Uncertainty in Analytical Chemistry” [16] and the ISO “Guide to the Expression of Uncertainty in Measurement (GUM)” for calculations [26].

Results and discussion

Inorganic ions were identified and quantified by IC under the operating conditions shown in Table 1. All ions under study were well resolved within a total run time of 12 min (Fig. 4). The identification and quantification of each ion were performed based on the retention time and peak area. The

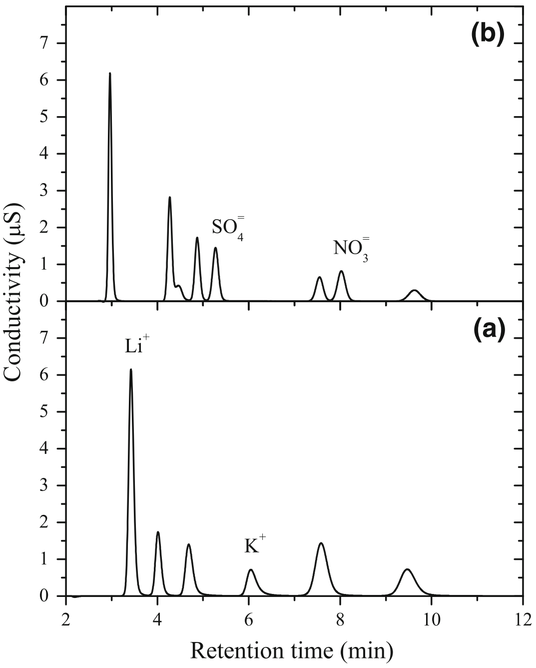

Fig. 4 The chromatogram for the cations (**a**) and anions (**b**) under study of the representative sample

retention times for the studied ions were 7.99, 5.25, 6.12, and 3.47 min for NO_3^-, SO_4^-, K^+, and Li^+, respectively.

Calibration curve

A standard curve for each anion under study was used to identify the concentrations at the corresponding retention time. The concentrations of the working calibration solutions for curves (c_j) in mg L^{-1}, the triplicate measurement average of the area under the peak (A_j) in μS min, and the relative standard deviations (RSD_j) in μS min are shown in Table 2. The retention times, calibration concentration range, slope, and coefficient of correlation for studied ions are shown in Table 3. For all ions, a good linear correlation fit was found ($r^2 > 0.997$) and the detection limits were suited for the study, see an example in Fig. 5.

Repeatability study

The descriptive statistics and reproducibility data of the peak areas for the target inorganic ions in representative samples are given in Table 4. The reproducibility was expressed as RSD. None of the RSD values of the target anion concentrations (Table 4) exceeded 22%. The study can also be performed using different concentration ranges, but only the range appropriate for the expected atmospheric levels of the target ions in the city of Santiago was used in this study.

Recovery study

The recovery studies were performed by spike to extract samples of particulate matter (Table 4). The column labeled *means* in Table 4 is the average of four injections and the *theoretical* column corresponds to the amount of added certified reference solution that was kept within the range of the calibration limits. From Table 4, we can conclude that quantitative recovery, calculated according to Eq. 14, ranged from 98 to 110% for the ions under study.

Air sampling volume

Table 5 shows the magnitudes of the influence for estimating the uncertainty of the air sampling according to Eq. 7.

Table 2 Data of the calibration curve concentration (c_j) in mg L^{-1}, peak area A_j in μS min, and standard deviation (SD) in μS min

c_j (mg L^{-1})	NO_3^-		$SO_4^=$	
	A_j (μS min)	SD (μS min)	A_j (μS min)	SD (μS min)
0.2	0.035	0.012	0.061	0.025
0.5	0.095	0.015	0.132	0.028
1.0	0.203	0.045	0.248	0.056
3.0	0.495	0.001	0.721	0.102
5.0	0.853	0.042	1.188	0.115
7.0	1.203	0.110	1.602	0.151
10.0	1.749	0.143	2.295	0.172
	K^+		Li^+	
0.2	0.045	0.018	0.171	0.012
0.5	0.114	0.009	0.429	0.022
1.0	0.190	0.018	0.879	0.035
3.0	0.587	0.055	2.706	0.199
5.0	0.914	0.021	4.465	0.167
7.0	1.233	0.014	6.233	0.263
10.0	1.772	0.030	8.886	0.304

Table 3 Retention times and the important parameters for calibration curves: range of concentration, slope, and correlation coefficient

	Anion		Cation	
	NO_3^-	$SO_4^=$	K^+	Li^+
Retention time (min)	7.99	5.25	6.12	3.47
Concentration range (mg L^{-1})	0.2–10	0.2–10	0.2–10	0.2–10
Slope (μS L mg^{-1})	0.195	0.221	0.180	0.888
Coefficient of correlation, r^2	0.997	0.998	0.997	0.999

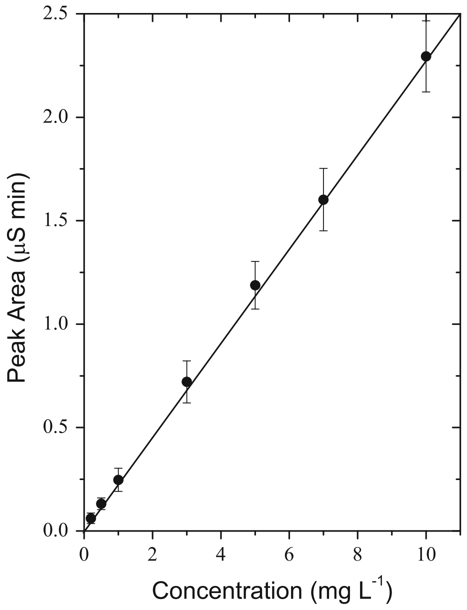

Fig. 5 Example calibration curve for concentration sulfate ions by ionic chromatography

Combined and expanded uncertainty

An evaluation of the contributions from individual uncertainty components made it possible to estimate the combined (Eq. 16) and expanded uncertainty (Eq. 17). The uncertainty in the result calculated using the proposed methodology is shown in Table 4. The expanded uncertainties calculated were less than 26% for all studied ions (Table 6).

Conclusion

This paper presents a detailed measurement equation and develops a full uncertainty budget for the analysis of anions and cations in real samples of particulate matter. The results of the overall expanded uncertainty estimations for the measurements of all studied ions are useful for the analysis of particular matter by IC. In addition, the results expressed as relative variation coefficients corresponded to 14.35, 19.53, 24.9, and 25.1% for Li^+, K^+, NO_3^-, and SO_4^-, respectively, calculated using a coverage factor equal to 2 at a level of confidence of 95%.

An examination of the uncertainty budget has revealed:

- The largest contributions to the combined uncertainty, in all cases, are derived from the uncertainty of the repeatability value which clearly indicates the great importance of IC analysis and the instrumental condition for uncertainty estimation. The contributions of the repeatability to the combined uncertainty were 48, 67, 48, and 24% for Li^+, K^+, NO_3^-, and SO_4^-, respectively.

Table 4 Descriptive statistics to reproducibility data for the target inorganic anions and cations in samples and recovery of the spiked samples ($n = 4$)

	Reproducibility				Recovery (R)			
	Means (mg L^{-1})[a]	n[b]	SD (mg L^{-1})[c]	RSD (%)[d]	Means $\bar{C}_{\text{obs}}(C_M)$ (mg L^{-1})[e]	n[b]	SD (mg L^{-1})[c]	R
NO_3^-	0.614	31	0.019	3.15	5.417 (5.80)	4	1.050	1.07
$SO_4^=$	0.081	23	0.017	21.4	5.341 (5.24)	4	0.261	0.98
K^+	0.053	21	0.011	21.2	4.944 (4.98)	4	0.216	1.01
Li^+	0.085	33	0.005	5.44	5.178 (5.18)	4	0.148	1.00

[a] Means concentration of reproducibility study

[b] Replicates number

[c] Standard deviation

[d] Relative standard deviation

[e] Means concentration of recovery study (C_{obs}) and reference value (C_M)

Table 5 Uncertainty in the sampling volume

		Value ± uncertainty	Unit
Flow volume of the sampling	V_f	$6.723\times10^{-3} \pm 0.002\times10^{-3}$	m^3 min^{-1}
Ambient temperature	T_a	19.73 ± 0.42	°C
Sampling pressure	P_a	93326 ± 116	Pa
Sampling time	t_s	10.0 ± 0.2	min
Flow reproducibility factor	f'_p	19.390 ± 0.003	m^3
Flow tolerance factor	f'_o	0.10 ± 0.06	m^3
Air sampling volume	V_a	16.72 ± 0.46	m^3

Table 6 Uncertainty budget for anions and cations under study

Influence magnitude	u_{standard}	Unit
Anion		
NO_3^-		
Analytical function		
Analytical response	251×10^{-6}	$\mu g\ L^{-1}$
Tolerance	783×10^{-6}	$\mu g\ L^{-1}$
Calibration	170×10^{-6}	$\mu g\ L^{-1}$
Repeatability	4.75	$\mu g\ L^{-1}$
Recovery	0.809	$\mu g\ L^{-1}$

	Value	u_{standard}	Unit
Concentration	81.5	10	$\mu g\ L^{-1}$
Air volume	16.72	0.021	m^3
Extraction volume	0.50	5.5×10^{-3}	L

	Value	u_{combined}	Unit
Concentration in air	3.05	0.384	$\mu g\ m^{-3}$

The result expressed with the expanded uncertainty, calculated using a coverage factor $k = 2$, at level of confidence of 95%, is: $(3.05 \pm 0.77)\ \mu g\ m^{-3}$

The uncertainty correspond to: 25.2%

Influence magnitude	u_{standard}	Unit
$SO_4^{=}$		
Analytical function		
Analytical response	−1.18	$\mu g\ L^{-1}$
Tolerance	−1.1	$\mu g\ L^{-1}$
Calibration	0.207	$\mu g\ L^{-1}$
Repeatability	11.3	$\mu g\ L^{-1}$
Recovery	2.55	$\mu g\ L^{-1}$

	Value	u_{standard}	Unit
Concentration	384	48	$\mu g\ L^{-1}$
Air volume	16.72	0.021	m^3
Extraction volume	0.50	5.5×10^{-3}	L

	Value	u_{combined}	Unit
Concentration in air	14.35	1.801	$\mu g\ m^{-3}$

The result expressed with the expanded uncertainty, calculated using a coverage factor $k = 2$, at level of confidence of 95%, is: $(14.35 \pm 3.68)\ \mu g\ m^{-3}$

The uncertainty correspond to: 25.1%

Influence magnitude	u_{standard}	Unit
Cations		
K^+		
Analytical function		
Analytical response	0.085	$\mu g\ L^{-1}$
Tolerance	1.95	$\mu g\ L^{-1}$
Calibration	0.494	$\mu g\ L^{-1}$
Repeatability	21.90	$\mu g\ L^{-1}$
Recovery	0.593	$\mu g\ L^{-1}$

	Value	u_{standard}	Unit
Concentration	337	32.7	$\mu g\ L^{-1}$
Air volume	16.72	0.021	m^3
Extraction volume	0.50	5.55×10^{-3}	L

	Value	u_{combined}	Unit
Concentration in air	12.59	1.230	$\mu g\ m^{-3}$

The result expressed with the expanded uncertainty, calculated using a coverage factor $k = 2$, at level of confidence of 95%, is: $(12.59 \pm 2.55)\ \mu g\ m^{-3}$

The uncertainty expressed like a relative coefficient of variation correspond to: 19.53%

Influence magnitude	u_{standard}	Unit
Li^+		
Analytical function		
Analytical response	0.109	$\mu g\ L^{-1}$
Tolerance	0.808	$\mu g\ L^{-1}$
Calibration	0.16	$\mu g\ L^{-1}$
Repeatability	3.35	$\mu g\ L^{-1}$
Recovery	0.107	$\mu g\ L^{-1}$

	Value	u_{standard}	Unit
Concentration	99.00	7.02	$\mu g\ L^{-1}$
Air volume	16.72	0.021	m^3
Extraction volume	0.5	5.5×10^{-3}	L

	Value	u_{combined}	Unit
Concentration in air	3.700	0.265	$\mu g\ m^{-3}$

The result expressed with the expanded uncertainty, calculated using a coverage factor $k = 2$, at level of confidence of 95%, is: $(3.70 \pm 0.57)\ \mu g\ m^{-3}$

The uncertainty correspond to: 14.35%

- The other uncertainty sources (analytical function recovery and extraction volume) had smaller contributions to the combined uncertainty, i.e., less than 76% in all studied cases.
- In the work of Brown and Edwards [35], a generic analysis of the uncertainty of an anion obtained a relative expanded uncertainty of approximately 12% assuming a coverage factor of $k = 2$ at the 95% confidence interval. In contrast, we found an uncertainty of approximately 25%, considering the same coverage factor and confidence interval. This difference arose because our work

considered other uncertainty sources, such as the volumetric measurement and estimation of the uncertainty from calibration. These differences clearly indicate the necessity of the harmonization of the methodologies to evaluate the uncertainty.

- Some studies suggest that some volatilization losses may occur during storage and especially for NO_3^- and SO_4^-. This may introduce an artifact bias in measurement, which also depends on the sampling device used, particle size fraction, the composition of aerosol, the chemical form of reactive species, duration of the sample storage, and the analytical technique used [35, 36]. However, removing samples soon after sampling, storing them in sealed containers under refrigeration, and keeping them in coolers for transport between the sampling site and laboratory and proper preservations should follow in laboratory can minimize this bias. In the present work, an analysis of the implications of the artifacts in uncertainty was not included.

The uncertainty (i.e., a deviation range (or interval) from a reported measurement result with corresponding probability) may be evaluated, but it is not possible to obtain a perfect (error-free) measurement and it not possible to estimate results with 100% probability (absolute certainty is also impossible). However, under well-controlled conditions and well-understood measurement processes and procedures, it is possible to minimize and relatively accurately estimate the uncertainties of measured quantities and the final measurement result.

Acknowledgments This effort was conducted under the Centro de Ciencias Ambientales, Facultad de Ciencias, Universidad de Chile and Centro Nacional del Medio Ambiente agreement. The authors are grateful to Dra. Isel Cortes for his helpful comments. I would also like to thank the anonymous reviewers for their useful recommendations that improved this manuscript.

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