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Evaluation of the performance of the determination of anions in the water soluble fraction of atmospheric aerosols

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ABSTRACT

The knowledge of the mass of particulate matter in air, its chemical composition and emission sources is of relevance for taking decisions concerning air quality management in urban areas. The interpretation of these data is a function of the quality of the measurement results expressed by their uncertainties.

This study aimed at developing models of the performance of the determination of anions in the water-soluble fraction of atmospheric aerosols, capable of determining, separately, the contribution of aerosols sampling, extraction of water-soluble fraction of atmospheric aerosols and quantification, by ion chromatography, of anions in the extract. The sampling procedure was assessed from the dispersion of results of duplicate parallel sampling after subtracting the analytical component of this dispersion. These models are used to evaluate the adequacy of the measurement procedure for the determination of urban aerosol composition and to support strategies for reducing measurement uncertainty or cost of analysis. The method performance was studied for the following ranges considering extract dilution up to five times: 0.23–8 $\mu g\ m^{-3}$ for chloride and nitrate, and 0.093–3.25 $\mu g\ m^{-3}$ for sulphate. Measurements are fit for the analysis of urban aerosols since the relative expanded measurement uncertainty is smaller than a maximum value of 40%. The percentage contribution of the uncertainty components varies with the analyte and its mass concentration, the major components being 24–93% for the extraction, 43–59% for sampling, 0.2–28% for the interpolation of the sample signal in the calibration curve and 4–8% for air volume measurement. The typical composition of analysed air is: $(1.12 \pm 0.26)\ \mu g\ m^{-3}$, $(1.02 \pm 0.30)\ \mu g\ m^{-3}$ and $(0.76 \pm 0.22)\ \mu g\ m^{-3}$ of chloride, nitrate and sulphate in the water soluble fraction of aerosol, respectively, for a confidence level of approximately 95% considering a coverage factor of 2.

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1. Introduction

Air composition, in terms of both gases and aerosols, is known to affect human-health. Hence, there is the need to perform measurements that provide relevant information about air quality. The European Directive 2008/50/EC [1] defines rules for ambient air monitoring programmes and sets limit values for particulate matter and some gaseous air components. This legislation also suggests assessing the origin of air pollution to infer which contaminants are expected to be present and should be tested.

Since the assessment of the compliance of ambient air with legislation or the evaluation of spatial or temporal differences in air composition depend on measurement quality, air composition data should be reported with respective uncertainty. Only when difference in estimated air composition with a limit value or between different air masses cannot be explained by measurement uncertainty, should be considered physical–chemical meaningful. Directive 2008/50/EC [1] defines maximum measurement uncertainty for assessing compliance with defined limit or target values. In this directive, for measurements of some contaminants (namely, sulphur dioxide, nitrogen dioxide, oxides of nitrogen, carbon monoxide, benzene, particulate matter, lead, ozone and related NO and NO_2), maximum measurements uncertainty of 15–25% or 25–50% of limit or target values of the contaminant for fixed and indicative measurements, respectively, are defined. Quality requirements of indicative measurements are less strict than for fixed measurements used to access higher levels of pollutants.

The measurement uncertainty is known to result from the combined effect of various individual components [2]. The identification and separate quantification of the uncertainty components allows recognition of major contributions, so that procedures can be developed to reduce them, thus increasing the quality of results. This information can also be used for cost of analysis reduction by identifying minor uncertainty components that can be managed with fewer resources (e.g., use of cheaper and more uncertain volumetric equipment).

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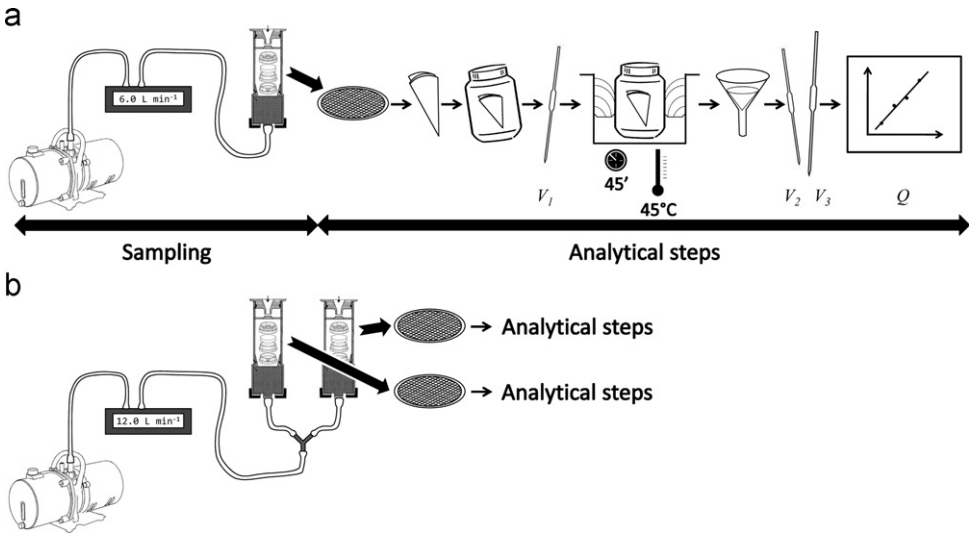

Fig. 1. Schematic representation of (a) the measurement procedure of the concentration of anion in the water-soluble fraction of atmospheric aerosols and (b) the measurement procedure used for estimating global measurement repeatability, s'_G (see glossary for notation).

In this work, a measurement procedure for the determination of anions in the water-soluble fraction of atmospheric aerosols is implemented and validated. This measurement procedure is based on active sampling of aerosols onto filters, followed by extraction with water, under defined conditions, and analysis of anions in the extracts by ion chromatography (Fig. 1a).

This work aims at developing a model of the measurement performance for assessing its adequacy for the analysis of urban aerosols and supporting needed performance improvements and/or cost of analysis reduction. The performance of all analytical steps, including sampling and filter extraction, are accessed separately. Air sampling is known to be a critical stage of these measurements [3].

The developed measurement procedure, including the measurement uncertainty, is applicable to the analysis of air in sites where air quality is, expectedly, representative of an area. Directive 2008/50/EC [1] describes how to proceed to guarantee the representativeness of air sampling. The uncertainty associated with the heterogeneity of the represented area is not considered in this work since measures can be implemented to reduce its impact on air quality evaluation and, whenever this effect is relevant, it varies with the specific problem faced.

The evaluation of the performance of the complex analytical steps (known to be difficult to model separately), namely sampling and filter extraction, was performed using the differential approach of the evaluation of the measurement uncertainty [4]. This approach involves the following stages: (1) quantification of the standard deviation of measurements precision, s; (2) estimation of the combined uncertainty of modelled uncertainty components, u_{Inc}, (3) estimation of complex (not previously modelled) uncertainty components by difference between s and u_{Inc}; (4) development of a model of the global measurement uncertainty [4]. The magnitude of various complex uncertainty components can be quantified, separately, by estimating the precision at different stages of the measurement [4].

In this work, intralaboratory reproducibility (intermediate precision in the latest edition of the International Vocabulary of Metrology [2]) of measurements excluding sampling was used to developed models of the analytical steps. These models together with the measurement repeatability, including the sampling stage, were used to estimate the sampling uncertainty by difference. The measurement repeatability was estimated from results of duplicate parallel sampling.

The developed models estimate measurements performance for a continuous mass concentration range of anions in the water soluble fraction of aerosols, assuming that the relative uncertainties of extraction and sampling are constant in the studied range.

2. Materials and methods

2.1. Sampling

The sampling system was placed on the roof terrace of the 4th floor of C8 building of the Faculty of Science of the University of Lisbon, Portugal.

Aerosols were sampled, using Gent type samplers, onto Whatman® 41 filters of 47 mm diameter collecting particulate matter with aerodynamic diameters smaller than 1 μm (PM_1). The measurement repeatability was studied from results of 10 parallel and simultaneous samplings performed by two parallel samplers, positioned at a distance of 15 cm, connected to the same air pump (Fig. 1b). The sampling was performed over 24-h periods of 10 consecutive days at a flow rate, θ, of 6 L min^{-1} (the pump was operating at 12 L min^{-1}). The geometry of air splitting device was tested by measuring air flow after each filter. Since air flow readings are the same in both branches, the air splitting differences were considered negligible.

2.2. Measurements of anions in the water soluble fraction of aerosols

Each sampled filter was placed in a 15 mL PTFE bottle to which 10 mL (V_1) of ultrapure water were added. The capped bottles were sonicated for (45 ± 2) min at a temperature of (45 ± 1) °C after which the extract was cooled to room temperature and filtered through a Whatman® 41 filter. The control of the extraction temperature aimed at keeping extraction efficiency independent of room temperature. The sample extract was diluted, when needed, by adding a volume V_3 of water to a volume V_2 of the extract, and analysed by ion chromatography (IC). Volumetric measurements were performed with Class A glassware.

3. Theory

3.1. Validation of the measurement procedure

The validation of the measurement procedure involved collecting information about the measurement performance, in the analytical range, and assessing its adequacy considering the intended use of measurements.

The measurement procedure validation included the following stages: (1) assessment of the repeatability of ion chromatographic measurements, (2) assessment of the adequacy of the IC calibration model, (3) assessment of the intralaboratory reproducibility of the analytical measurements (i.e., measurement procedure excluding sampling), (4) assessment of repeatability of the global measurement and (5) evaluation of the measurement uncertainty.

The following sections describe the experiments and calculations performed in these stages and present the used performance criteria.

3.1.1. Assessment of the repeatability of IC measurements

The relative standard deviation of the repeatability of IC measurements, s'_Q, is estimated from the standard deviation of the relative differences, s'_d,($s'_Q = s'_d/\sqrt{2}$) of results of duplicate injections of 20 extracts, each duplicate being analyzed in repeatability conditions (the apostrophes stands for relative quantities). The s'_Q is considered satisfactory if not larger than 5%.

3.1.2. Assessment of the adequacy of the IC calibration model

The adequacy of the linear unweighted regression model to describe the variation of IC signal with anion concentration was tested by checking the validity of the assumptions of this regression model, namely: (i) homoscedasticity of the standard deviation of the repeatability of signals through the calibration range (tested with an *F*-test for a confidence level of 99%); (ii) negligible uncertainty associated with the ratio of the concentrations of the calibration standards [5] and (iii) linearity of variation of IC signal in the calibration range (tested with ANOVA lack-of-fit test for a confidence level of 99%) [6].

The critical values of the statistical tests are the used performance criteria.

3.1.3. Assessment of the intralaboratory reproducibility of analytical measurements

The relative standard deviation,s'_A, of the intralaboratory reproducibility of the measurement results excluding sampling stage was estimated from the concordance of results of the analysis, in different days, of pair of filters obtained from the cross changing of their halves. Since perfectly homogeneous pairs of filters are not possible to obtain, several pairs of filters, from air sampling performed in Lisbon, were cut in halves and their pieces cross changed producing a pair of combined filter with equivalent aerosol composition. The impact of the symmetry of filter cutting in the equivalence of produced filters was assessed from the mass of each halve. For each pair of combined filters, the relative difference of the mass of anions in the water soluble fraction of aerosols was estimated. The standard deviation of the relative difference of various pairs of filters and the uncertainty introduced by filter cutting symmetry was used to estimate the intralaboratory reproducibility of analytical measurements [6]. The possible heterogeneity of the deposition of aerosol in the filter is taken into account, in the developed strategy of the evaluation of the measurement uncertainty, since it increases the magnitude of s'_A.

The assessment of the magnitude of the intralaboratory reproducibility of the analytical measurements is included in the evaluation of the measurement uncertainty. Therefore, no specific criterion for s'_A was defined.

3.1.4. Assessment of the repeatability of the global measurement

The relative repeatability of the global measurement, s'_G, excluding air volume measurements, is estimated by the standard deviation of the relative difference of results of the mass of anions in the water soluble fraction of aerosol from parallel collections (Section 2.1). The standard deviation of the relative difference is square root of two times larger than the relative standard deviation of the repeatability of single measurements.

3.1.5. Evaluation of the measurement uncertainty

This section is divided in the evaluation of the uncertainty associated with analytical steps and the evaluation of the global measurement uncertainty including the evaluation of sampling and air volume measurement uncertainties.

3.1.5.1. Uncertainty associated with the analytical steps. The intralaboratory reproducibility of the analytical measurements, estimated from the analysis of pairs of filters obtained by cross changing their halves, was compared with the modelled uncertainty components affecting the estimated intralaboratory reproducibility, aiming at estimating the extraction uncertainty by difference. This evaluation is described elsewhere [6]. The outcomes of this research are models of the performance of all analytical steps and a model of the combination of these components. The performance of the analytical steps is fit for the intended use since their relative expanded uncertainty is not larger than a maximum value of 30% [6].

3.1.5.2. Global measurement uncertainty. The evaluation of the measurement uncertainty is divided in steps extensively described in the literature [7,8].

(i) Definition of the measurand and of the model function:
The measurand, *M*, is the concentration of an anion in the water-soluble fraction of PM_1 particles in a specific air volume estimated by measurement procedure previously described. This procedure includes the sampling and analytical steps. Eq. (1) presents the used model function:

$$M = \frac{Q \times V_1 \times (V_2+V_3)/V_2}{\theta \times t \times (P_c \times T_s)/(T_c \times P_s)} = \frac{Q \times V_1 \times F_{\mathrm{dil}}}{\zeta} \quad (1)$$

where Q is the concentration of anion in the diluted extract,θ is the air flow rate measured in the flowmeter, P_s is the average pressure during the sampling, P_c is the pressure during flowmeter calibration, T_s is the average temperature during air sampling, T_c is the temperature during flowmeter calibration, t is the sampling time, ζ is the sampled air volume corrected for its temperature and pressure using the ideal gas law [9] and F_{dil} is the extract dilution factor $[(V_2+V_3)/V_2]$.
Since Eq. (1) does not explicitly reflect the impact of sampling and analytical extraction in measurement uncertainty, two additional unitary factors must be included, F_s and F_{ext}, respectively.

$$M = \frac{F_s \times F_{\mathrm{ext}} \times Q \times V_1 \times (V_2+V_3)/V_2}{\theta \times t \times (P_c \times T_s)/(T_c \times P_s)} = \frac{F_s \times F_{\mathrm{ext}} \times Q \times V_1 \times F_{\mathrm{dil}}}{\zeta} \quad (2)$$

Unitary factors are multiplying factors equal to one introduced in the original model function (in this case Eq. (1)) to reflect the impact of an uncertainty effect not directly

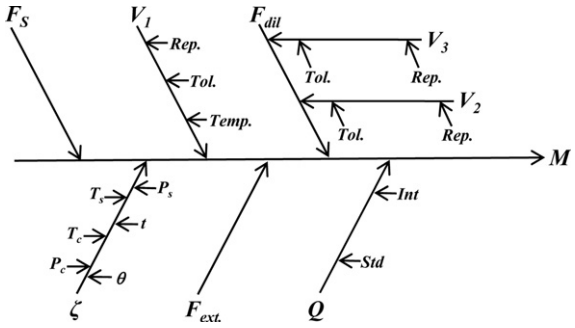

Fig. 2. Cause and effect diagram representing the identified sources of uncertainty (see glossary for notation); Rep.—repeatability; Tol.—calibration component; Temp.—temperature effect.

linked to the original variables. F_s and F_{ext} will be associated with a standard uncertainty reflecting sampling and extraction efficiency uncertainties. The value one for F_s and F_{ext} guarantees no impact in the measured quantity value (i.e., best estimation of the measurand). The updated model function (in this case Eq. (2)) allows to understanding how uncertainty associated with unitary factors should be combined with one affecting original variables.

(ii) Identification of the sources of uncertainty:
Fig. 2 presents the cause and effect diagram representing the identified sources of uncertainty.
The input quantities of Eq. (2), are divided in specific effects. All volumetric operations are affected by the repeatability of the volumetric material manipulation (Rep.) and nominal value tolerance (Tol.). The single volumetric measurement V_1, is also affected by the temperature effect (Temp.). The estimated concentration of the diluted extract (Q) is affected by the uncertainty associated with calibration standards concentration (Std) and statistical interpolation of the sample signal in the calibration curve (Inter) [5].

(iii) Quantification of the sources of uncertainty:
- Volumetric measurements
The uncertainty components affecting volumetric measurements were quantified as proposed in the Eurachem/CITAC guide [8]. The uncertainty associated with the F_{dil}, $u_{F_{dil}}$, was estimated using the uncertainty propagation law:

$$u_{F_{dil}} = \sqrt{\left(-\frac{V_3}{V_2^2}\right)^2 u_{V_2}^2 + \left(\frac{1}{V_2}\right)^2 u_{V_3}^2} \quad (3)$$

where u_{V_2} and u_{V_3} are standard uncertainties associated with V_2 and V_3, respectively.
- Concentration of the diluted extract
The relative standard uncertainty,u'_Q, associated with Q, results from the combination of the relative standard uncertainties associated with calibration standard, u'_{Std}, and associated with the interpolation of the sample signal in the calibration curve u'_{Int}.

$$u'_Q = \sqrt{(u'_{Std})^2 + (u'_{Int})^2} \quad (4)$$

The u'_{Std} is equivalent to the relative standard uncertainty associated with the concentration of the stock solution from which calibrations standards are diluted with a negligible uncertainty. The u'_{Int} is the relative standard deviation of the statistical interpolation of the sample signal in the calibration curve estimated by the linear unweighted regression model [5].
- Extraction of anion from the filter
The relative standard uncertainty associated with F_{ext}, u'_{ext}, was estimated by difference between the relative standard deviation of the intralaboratory reproducibility of analytical measurements, s'_A, and the precision components know to affect this precision except the extraction itself.

$$u'_{ext} = \sqrt{(s'_A)^2 - \left[\left(s'_{F_{dil}}\right)^2 + \left(s'_{V_1}\right)^2 + \left(s'_Q\right)^2\right]} \quad (5)$$

where s'_Q, $s'_{F_{dil}}$ and s'_{V_1} are standard deviations of the repeatability of IC signal, F_{dil} and V_1 estimated from the algorithms used to calculate the respective standard uncertainty where only precision components are considered.
- Sampling
The relative standard uncertainty associated with sampling,u'_S, is estimated by difference between the relative standard uncertainty associated with sampling and extraction, $u'_{S\&ext}$, and extraction separately, u'_{ext}. The $u'_{S\&ext}$ was estimated by difference between the s'_G and the precision components known to affect this repeatability except the sampling and extraction. This calculation is supported on the assumption that extraction repeatability and intralaboratory reproducibility are statistically equivalent whenever measurements are performed by the same analyst. Since extraction temperature and time are strictly controlled, the variability of the analyst manipulation of the filter and extract should be responsible for a major component of results variability. Eq. (6) is used to estimate $u'_{S\&ext}$:

$$u'_{S\&ext} = \sqrt{(s'_G)^2 - \left[\left(s'_Q\right)^2 + \left(s'_{F_{dil}}\right)^2 + \left(s'_{V_1}\right)^2\right]} \quad (6)$$

The u'_S is estimated from Eq. (7):

$$u'_S = \sqrt{(u'_{S\&ext})^2 - (u'_{ext})^2} \quad (7)$$

This difference is only meaningful and can be calculated if sampling uncertainty is not negligible. This condition can be checked through a one-tailed F-test, where $u'_{S\&ext}$ is tested to be larger than u'_{ext}.
- Sampled air volume
The relative standard uncertainty associated with the sampled air volume is estimated by Eq. (8).

$$u'_\zeta = \sqrt{(u'_\theta)^2 + \left(u'_{P_S}\right)^2 + \left(u'_{P_C}\right)^2 + \left(u'_{T_S}\right)^2 + \left(u'_{T_C}\right)^2 + (u'_t)^2} \quad (8)$$

where u'_i is the relative standard uncertainty associated with the variable i.

(iv) Combination of the uncertainty components
The uncertainty components were combined using the uncertainty propagation law (UPL):

$$u'_c = \sqrt{(u'_S)^2 + \left(u'_{V_1}\right)^2 + (u'_{ext})^2 + \left(u'_{F_{dil}}\right)^2 + \left(u'_Q\right)^2 + \left(u'_\zeta\right)^2} \quad (9)$$

(v) Expansion of the combined standard uncertainty
Since combined standard uncertainty is associated with a high number of degrees of freedom, a coverage factor of 2 is used to expand the confidence level to 95%. This condition was tested by combining the degrees of freedom

associated with the uncertainty components using Welch–Satterthwaite formula [7]. The degrees of freedom associated with type B evaluations were estimated as proposed in the ISO-GUM [7].

(vi) Assessment of the magnitude of the measurement uncertainty

Since, for the studied analytes, no limit or maximum measurement uncertainty values are set in Directive 2008/50/EC [1], quality requirements defined in this legislation for indicative measurements of contaminants are considered for assessing fitness of performed measurements for the characterisation of urban aerosols. This directive defines that indicative measurements should be affected by an expanded uncertainty not larger than 25–50% of the limit or target value, suggesting an increase in maximum relative measurement uncertainty as concentration decreases. Therefore, considering this criterion, a maximum relative measurement uncertainty of 40% was defined for the studied analytes and concentration ranges. This value is smaller than the defined for indicative measurements of particulate matter next to the limit value. This criterion establishes indirect limits to the observed measurement repeatability and intralaboratory reproducibility.

4. Results and discussion

This section is divided in two parts, the presentation of results of the validation of the measurement procedure excluding the evaluation of the measurement uncertainty, and the evaluation of the measurement uncertainty including an example of calculations performed for the analysis of a sample. The studied concentration ranges of anion mass in the water-soluble fraction of aerosol in air volume, considering an extract dilution up to five times, are 0.23–8 μg m^{-3} for chloride and nitrate ions and 0.093–3.25 μg m^{-3} for sulphate ion.

4.1. Validation of the measurement procedure

4.1.1. Repeatability of IC measurements

The relative standard deviation of the repeatability of IC measurements, s'_Q, for the calibration ranges were 2.264%, 2.383% and 2.065% for chloride, nitrate and sulphate, respectively.

4.1.2. Adequacy of the IC calibration model

The linear unweighted regression model proved to be adequate to describe the IC calibration ranges: 0.20–1.40 mg L^{-1} for chloride and nitrate and 0.0801–0.560 mg L^{-1} for sulphate.

4.1.3. Intralaboratory reproducibility of analytical measurements

The relative standard deviation of the intralaboratory reproducibility of analytical measurements, s'_A, is 11.45%, 13.34% and 9.208% for chloride, nitrate and sulphate, respectively.

4.1.4. Repeatability of global measurements

The relative standard deviation of the repeatability of global measurements, s'_G, is 9.881%, 13.22% and 13.96% for chloride, nitrate and sulphate, respectively.

4.2. Evaluation of the measurement uncertainty.

This section presents the results of the quantification and combination of the uncertainty components, and the expansion of the combined standard uncertainty.

Table 1
Relative standard deviation, expressed in percentage, of components involved in the calculation of the relative standard uncertainty associated with the extraction of anions from filters, u'_{ext}.

Analyte	S'_A	s'_{V_1}	$s'_{F_{dil}}$	S'_Q	u'_{ext}
Chloride	11.4	0.0191	0.122	2.98	11.0
Nitrate	13.3	0.0191	0.122	2.68	13.1
Sulphate	9.21	0.0191	0.122	4.11	8.24

Table 2
Relative standard uncertainty, expressed in percentage, of components involved in the calculation of the relative standard uncertainty associated with the sampling of anions in filters, u'_S.

Analyte	S'_G	s'_{V_1}	u'_{ext}	$s'_{F_{dil}}$	S'_Q	$u'_{S\&ext}$	u'_S
Chloride	9.88	0.0191	11.0	0.198	2.26	9.61	ng
Nitrate	13.2	0.0191	13.1	0.198	2.38	13.0	ng
Sulphate	14.0	0.0191	8.24	0.198	2.06	13.8	11.1

ng—negligible uncertainty component.

Table 3
Relative standard uncertainty, expressed in percentage, associated with input quantities and output quantity.

Analyte	u'_S	$u'_{\bar{s}}$	u'_{V_1}	u'_{ext}	$u'_{F_{dil}}$ [b]	u'_{Std}	u'_{Int} [a]	u'_c [a]
Chloride	ng	2.56	0.237	11.0	0.360	0.674	0.875–6.42	11.6–13.2
Nitrate	ng	2.56	0.237	13.1	0.360	0.850	0.579–4.04	13.5–14.1
Sulphate	11.1	2.56	0.237	8.24	0.360	1.62	1.37–9.00	14.4–16.9

ng—negligible uncertainty component.

[a] Maximum and minimum values within the concentration range of a specific calibration curve.

[b] Relative standard uncertainty for $F_{dil}=3=(1+2)/1$.

Table 1 presents the precision components involved in the calculation of u'_{ext}. Extracts were diluted by adding 1 mL of water to 1 mL of extract.

4.2.1. Evaluation of the uncertainty associated with sampling

Table 2 presents the components of Eqs. (6) and (7) used to calculate the relative standard uncertainty of sampling, u'_S.

The $u'_{S\&ext}$ is statistically larger than u'_{ext} only for sulphate. Therefore, sampling uncertainty is negligible for nitrate and chloride. The significance of sampling uncertainty of sulphate can be attributed to the smaller concentration of this anion that can be more affected by the heterogeneity of air composition.

The negligible contribution of sampling uncertainty to the global uncertainty does not suggest u'_S is zero for these analytes. The statistical equivalence of $u'_{S\&ext}$ and u'_{ext}, inferred considering the degrees of freedom associated with these standard uncertainties, hides a quantitative value of u'_S. Nevertheless, this not null uncertainty component would not affect significantly the global measurement uncertainty and, therefore, does not need to be quantified.

4.2.2. Global measurement uncertainty model

Table 3 presents the standard uncertainty of all uncertainty components affecting significantly measurement quality. These uncertainty components include both components associated with measurement bias and precision.

Since the uncertainty associated with the interpolation of the sample signal in the calibration curve varies with the

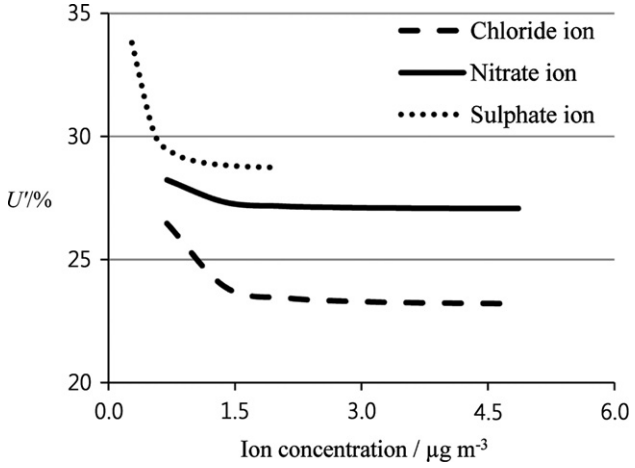

Fig. 3. Variation of the relative expanded measurement uncertainty, U', with the concentration of anion (chloride, nitrate or sulphate) in water-soluble fraction of atmospheric aerosols. These lines were estimated considering a specific calibration curve and a dilution of 1 mL of extract by adding 2 mL of purified water ($F_{dil}=3$). These curves are not significantly affected by daily variation of the IC repeatability.

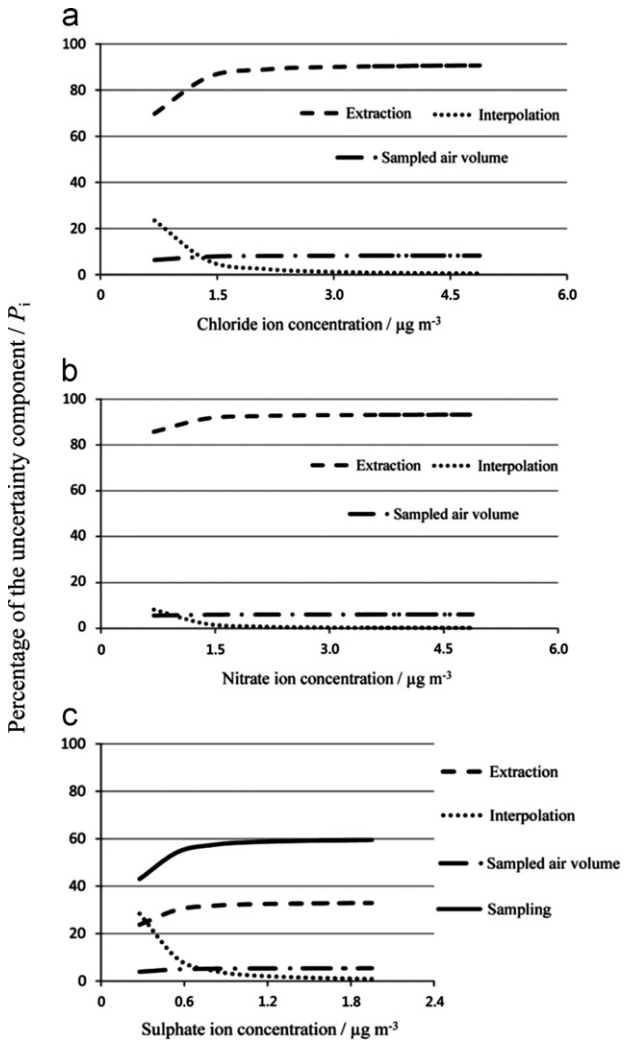

Fig. 4. Variation of the percentage contribution of major uncertainty components (sampling, sampled air volume, extraction and interpolation of the sample signal in the calibration curve) with the concentration of anion [(a) chloride, (b) nitrate and (c) sulphate] in the water soluble fraction of atmospheric aerosols. These lines were estimated considering a specific calibration curve and a dilution of 1 mL of extract by adding 2 mL of purified water ($F_{dil}=3$). These curves are not significantly affected by daily variation of the IC repeatability.

concentration range, an interval with the maximum and minimum uncertainty value for a specific calibration curve is presented. These values slightly vary with daily variations of the instrumental precision.

Since the number of degrees of freedom of performed estimations is between 18 and 32, it can be concluded that the coverage factor of 2 adequately expands the combined expanded uncertainty to a confidence level of 95%.

Fig. 3 presents the variation of the relative expanded uncertainty, U', with the concentration of the three analytes considering $F_{dil}=3$. The trend of this curve is not significantly affected by dilution factor. It can be observed that U' decreases or is constant in the range, and presents values smaller than the maximum measurement uncertainty. Therefore, it can be concluded that measurements are fit for the analysis of urban aerosols.

Fig. 4 presents the percentage contribution, P_i, of major uncertainty component i, quantified by the relative standard uncertainty, u'_i, considering the way components are combined (Eq. 9): $P_i=(u'_i)^2/(u'_c)^2$. It can be observed that the relevance of the uncertainty components vary with analyte and concentration level.

For chloride, measurement uncertainty is dominated by the extraction component responsible for 70% to 91% of the global uncertainty. The uncertainty associated with the interpolation of the sample signal in the calibration curve is important at lower concentrations.

For nitrate, the extraction component is also dominant since it is responsible for 86% to 93% of the global uncertainty.

For sulphate, sampling is the larger uncertainty component (43–59%) whose contribution is equivalent to extraction one (24–33%). The interpolation of the sample signal in the calibration curve is a relevant uncertainty component at lower concentrations, reaching 28% of the global uncertainty.

Extraction uncertainty can be reduced by defining narrower tolerances of experimental parameters like extraction temperature. Sampling uncertainty can be reduced by using larger sampling times. The increase in sampling period also reduces the relative uncertainty associated with measured sampled volume. Since the magnitude of the measurement uncertainty is fit for the analysis of urban air, this optimization can only be useful for the characterisation of areas with highly homogeneous air composition. Since, in these specific example, the uncertainty associated with volumetric operations are negligible, the cost of analysis can be reduced by using lower quality volumetric ware, instead of Class A one, with negligible impact on measurement uncertainty.

Table 4
IC signals involved in the quantification of diluted extract of the analysis of sulphate in the water soluble fraction of aerosol collected as described in Section 4.2.3.

IC calibration			
Calibration standard (mg L^{-1} of SO_4)	Signal (peak area)		
	Replicate 1	Replicate 2	Replicate 3
0.0808	21,526	20,974	18,479
0.240	67,620	66,953	66,482
0.400	117,409	117,696	123,909
0.560	167,847	162,991	169,219
Intercept (signal)	−5110	–	–
Slope (L mg^{-1})	307443	–	–
Sample			
Signal (peak area)	91950	–	

Table 5
Input quantities and output quantity (final result) and respective standard uncertainties for the determination of sulphate in the water soluble fraction of aerosol in air analysis described in Section 4.2.3.

	Unit	Value	Standard uncertainty
Input quantity			
θ	L min^{-1}	6.00	0.15
P_c	kPa	101.35	0.10
T_c	K	294.25	0.25
P_s	kPa	103.24	0.10
T_s	K	287.05	0.25
T	min.	1440	2
F_s	–	1.00	0.11
V_1	mL	10.000	0.024
F_{ext}	–	1.000	0.082
V_2	mL	1.0000	0.0017
V_3	mL	1.0000	0.0017
Q	mg L^{-1}	0.3157	0.0092
Output quantity			
M	μ m^{-3}	0.76	0.11

4.2.3. Application example

This section presents an example of the application of the developed measurement model to the determination of sulphate in the water soluble fraction of aerosols collected in the sampling site, described in Section 2.1, between 09:00 h of February 9 and 09:00 h of February 10, 2012. Table 4 presents the signals collected during IC quantifications and Table 5 presents the values of the input quantities of Eq. (2) and respective standard uncertainties. In the bottom of this table, the measured quantity value and combined standard uncertainty are reported. The output quantity is associated with 26 effective degrees of freedom.

It can be observed from Table 5 that measurement result is fit for the intended use since it presents a relative expanded uncertainty, considering a coverage factor of two, (28%) smaller than 40%.

5. Conclusions

The differential approach for the evaluation of the measurement uncertainty was successfully applied to the development of models of the performance of the determination of anions in the water-soluble fraction of urban aerosol. The developed models include information of the performance of sampling and anion extraction from filters, separately, needed to develop adequate strategies for measurement uncertainty and/or cost of analysis reduction. The measurements are fit for the analysis of urban aerosols since they present a relative expanded uncertainty smaller than 40%. The extraction step has the most relevant uncertainty component for chloride and nitrate (70–93%) and is a major component for sulphate (24–33%). Sampling has the largest uncertainty component for sulphate (43–59%) being negligible for chloride and nitrate dominated by the extraction step. This information can be used to reduce the cost of analysis of urban air by using lower quality volumetric ware.

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Glossary

Acronyms

IC:: ion chromatography;
Inter:: statistical interpolation of the sample signal in the calibration curve;
PTFE:: polytetrafluoroethylene;
Rep:: repeatability;
Std:: calibration standards;
Temp:: temperature effect;
Tol:: tolerance;
UPL:: uncertainty propagation law for uncertainty components combination.

Symbols

θ:: measured air flow;
ζ:: sampled air volume;
F_{dil}:: dilution factor $[(V_2+V_3)/V_2]$;
F_{ext}:: unitary factor used to estimate the impact of the intralaboratory reproducibility of extraction in measurement uncertainty;
F_S:: unitary factor used to estimate the impact of sampling uncertainty in measurement uncertainty;
F_{std}:: unitary factor used to estimate the impact of calibration standards uncertainty in measurement uncertainty;
M:: concentration of anion in water-soluble fraction of aerosol of a specific air volume estimated by measurement procedure described in Sections 2.1 and 2.2;
P_C:: air pressure during flowmeter calibration;
P_i:: percentage contribution of the uncertainty component i;
P_S:: average air pressure during sampling;
Q:: concentration of anion in the diluted extract;
s'_A:: relative standard deviation of the intralaboratory reproducibility of analytical measurements;
s'_d:: standard deviation of the relative differences of duplicate IC signals of extracts obtained in repeatability conditions;
$s'_{F_{dil}}$:: relative standard deviation of the repeatability of F_{dil};
s'_G:: relative standard deviation of the repeatability of M measurements;
s'_Q:: relative standard deviation of the repeatability of ion chromatographic measurements;
s'_{V_1}:: relative standard deviation of the repeatability of V_1 measurements;
t:: sampling time;
T_C:: air temperature during flowmeter calibration;
T_S:: average of air temperature during air sampling;
U':: relative expanded measurement uncertainty;
u_c:: combined standard uncertainty;
u'_c:: relative combined standard uncertainty;
u'_{ext}:: relative standard uncertainty associated with the extraction of ions from filters;
$u'_{F_{dil}}$:: relative standard uncertainty of the dilution factor F_{dil};
u'_i:: relative standard uncertainty associated with i;
u'_{Int}:: relative standard uncertainty associated with the interpolation of the sample signal in the calibration curve;
u'_Q:: relative standard uncertainty associated with the Q;
u'_S:: relative standard uncertainty associated with the sampling;
$u'_{S\&ext}$:: relative standard uncertainty associated with combined effect of sampling and extraction of anions from filter;
u'_{Std}:: relative standard uncertainty associated with calibration standard concentration;
u'_{V_1}:: relative standard uncertainty of V_1 measurement;
u'_{V_2}:: relative standard uncertainty of V_2 measurement;
u'_{V_3}:: relative standard uncertainty of V_3 measurement;
V_1:: volume of aerosol extract;
V_2:: aliquot of aerosol extract subjected to dilution;
V_3:: volume of solvent added to V_2 for its dilution.