

Standardisation of a European measurement method for the determination of anions and cations in PM_{2.5} : results of field trial campaign and determination of measurement uncertainty

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Standardisation of a European measurement method for the determination of anions and cations in PM_{2.5}: results of field trial campaign and determination of measurement uncertainty

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European Committee for Standardisation (CEN) Technical Committee 264 'Air Quality' has recently produced a standard method for the measurements of anions and cations in PM_{2.5} within its Working Group 34 in response to the requirements of European Directive 2008/50/EC. It is expected that this method will be used in future by all Member States making measurements of the ionic content of PM_{2.5}. This paper details the results of a field measurement campaign and the statistical analysis performed to validate this method, assess its uncertainty and define its working range to provide clarity and confidence in the underpinning science for future users of the method. The statistical analysis showed that, except for the lowest range of concentrations, the expanded combined uncertainty is expected to be below 30% at the 95% confidence interval for all ions except Cl⁻. However, if the analysis is carried out on the lower concentrations found at rural sites the uncertainty can be in excess of 50% for Cl⁻, Na⁺, K⁺, Mg²⁺ and Ca²⁺. An estimation of the detection limit for all ions was also calculated and found to be 0.03 μg m⁻³ or below.

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Environmental impact

Particulate matter (PM) in ambient air remains a huge health concern. Compositional information on PM is essential to judge pollutant increments in more polluted areas (such as urban background, industry related locations, traffic related locations), assess the possible contribution from long-range transport of air pollutants, support source apportionment analysis and for the understanding of specific pollutants. As important indicators of secondary inorganic aerosol formation the measurement of anions and cations in PM is an important but challenging measurement. This study describes the development by group of European air quality reference laboratories of a standardised method for this measurement that will greatly improve the accuracy, stability and comparability of these measurements across Europe. The improved data produced using this method, which must be used by all EU Member States, will provide a better evidence base for more effective regulation to improve air quality.

1. Introduction

Air quality has always been an important issue for its effect on human health and the environment.^{1,2} The European

Commission is acting to reduce the exposure to a variety of pollutants across all Member States through European Air Quality Directive (Directive 2008/50/EC),³ which sets legally binding limits for concentrations of a number of pollutants, and the Fourth Air Quality Daughter Directive that sets targets for levels in outdoor air of certain toxic heavy metals and polycyclic aromatic hydrocarbons (Directive 2004/107/EC).⁴ In addition to the monitoring of particulate matter in the form of PM₁₀ and PM_{2.5}, the Directive 2008/50/EC, annex IV, requires the measurement of cations, anions, elemental and organic carbon (EC/OC) in PM_{2.5} in rural background areas. To be considered rural background area, the sampling point must not be significantly influenced by agglomerations, industrial sites or point sources. This compositional information is essential to judge pollutant increments in more polluted areas (such as urban background, industry related locations, traffic related

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locations), assess the possible contribution from long-range transport of air pollutants, support source apportionment analysis and for the understanding of specific pollutants such as particulate matter.⁵ The ions required to be measured are water soluble chloride (Cl^-), nitrate (NO_3^-), sulphate (SO_4^{2-}), sodium (Na^+), ammonium (NH_4^+), potassium (K^+), magnesium (Mg^{2+}) and calcium (Ca^{2+}).

To meet these requirements, enhance data quality, and ensure the stability and comparability of measurements made across Europe, the European Commission asked the European Committee for Standardisation (CEN)⁶ to develop standard methods for the measurements of particulate matter in ambient air and the measurement of its chemical composition (organic and elemental carbon, inorganic components). Although the analysis of sampled filters using ion chromatography has been the most used method for the measurements of ions in ambient air for a long time, there is currently no standard method available to Member States to meet the requirements of the European Directive and unify approaches across Europe. Other techniques like Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Atomic Absorption Spectroscopy (AAS) and photometry can also be used for the determination of certain cation concentrations from filters. CEN/TC 264/WG 34 "Anions/cations in $\text{PM}_{2.5}$ " has been responsible for the development of a European standard for the measurement of anions and cations in $\text{PM}_{2.5}$. This European Standard, EN 16913,⁷ describes a method for the determination of the mass of water soluble anions and cations in the $\text{PM}_{2.5}$ fraction validated by a combination of laboratory tests and the field trials described in this paper. (Whilst other sampling protocols are available⁸ this work specifically tested a protocol designed to meet the requirements of the European Air Quality Directive.⁹)

WG34 (in collaboration with WG35 who were standardising measurements of organic carbon and elemental carbon deposited on filters) conducted a field trial campaign to validate the draft standard method, set concentration ranges over which the method operated properly and determine measurement uncertainties (although no target uncertainties are addressed in the Directive 2008/50/EC for the measurements of EC/OC or ions in $\text{PM}_{2.5}$, this remains an important quality control criterion for valid measurement). This paper summarises the results of the field trial, using a novel statistical assessment of the results for field trials of this type, and uses this output to calculate the uncertainty and working range of the standard method. It is hoped that this will provide clarity and confidence in the underpinning science for future users of the method in a similar way to publication of previous studies supporting the validation of standard produced within CEN/TC 264.^{9,10} WG34 and WG35 collaborated on the field trial in order to keep costs to a minimum and also because in many Member States these two measurements are made from the same filter, again to minimise the costs of monitoring. Quartz fibre filters represent the best compromise as a filter type applicable to both measurements – particularly as they need to be robust enough to survive the high temperature applied during the EC/OC measurements. This filter type is expected to have acceptable

low blank values and sampling artefacts (for instance nitrate volatilisation) when anion and cation sampling is undertaken.

2. Field trial

Validation tests were performed around Europe during late 2013 and in 2014 at six locations with distinct and different pollution sources and climate conditions in order to get as much information as possible on the performance of the draft standard method under different conditions. The sites were chosen to represent different ambient conditions, sources and concentration levels expected across Europe. The field trial was carried out in parallel with the field trial for EC/OC conducted by CEN/TC264/WG35. The site operators were either members of both working group or members of WG35 only. The details of the field trial campaigns can be found in Table 1. Ideally some additionally sampling could have been carried out in Central and Eastern Europe but no offers for field trials at these locations were made. Nevertheless the different ambient conditions experienced by the field trial were deemed sufficient to properly assess the suitability of the proposed method.

Two Digital DHA-80 high volume samplers (HVS) fitted with a $\text{PM}_{2.5}$ head and sampling at $30 \text{ m}^3 \text{ h}^{-1}$ were available for the duration of the trial. At the first site (Ispra, Italy) and at the last site (Cabauw, the Netherlands) the two samplers were run in parallel. As explained later, this was done in order to get an estimation of a between-sampler effect in the overall uncertainty. At the end of the sampling period at the first site, the two samplers were separated and sent to the other locations for single sampler use and then co-located again at the last site of the field trial. Each sampler sampled for daily periods (from midnight to midnight) onto quartz filters (Pallflex® Tissuquartz™, 2500 QAT-UP, 150 mm). Field blank filters, *i.e.* filters that are transported to the site as the other filters but are not sampled, were used at all sites. The sampler bodies were either placed outdoors or in air-conditioned cabins (maintained at 20–22 °C). At the beginning of the trial and after transport from one site to the next one, the samplers were leak-checked and the flowrate was checked and adjusted if necessary.

After sampling, from each filter, including field blank filters, 6 punches were taken by the site operators using a 40 mm circular puncher and sent to 6 different laboratories. The punches were radially symmetrical and therefore deemed equivalent. The sub-samples were analysed using each laboratory's preferred analytical technique, but following the agreed protocol defined by the draft standard method, now adopted as the standard method: see ref. 7 for details. Table 2 reports the laboratories' details and the analytical techniques used. The sampling and the transport of the filters to and from the sites were carried out according to the European Standard EN 12341 (ref. 11) for the measurement of PM_{10} and $\text{PM}_{2.5}$. Standard operating procedures were implemented by the working groups for the operation of the HVS and for the filter handling.

The analysis results from each laboratory (expressed as mass of each ion per punch of filter) were sent to the National Physical Laboratory (NPL, UK) for statistical analysis. NPL calculated the final ambient concentrations using the sample volumes

Table 1 Details of the CEN/TC 264/WG34 field trial

Country	Italy	Spain	Germany	The Netherlands	Germany	The Netherlands
Site operator	JRC-IES Institute for Environment and Sustainability, European Commission	IDAEA-CSIC, Institute of Environmental Assessment and Water Research	UBA, German Federal Environment Agency	GGD, Health service in Amsterdam	IUTA, Institute of Energy and Environmental Technology	TNO, Netherlands Organisation for Applied Scientific Research
Site location and details	Ispra, Rural Background station located on the JRC-IES site, situated in a semi-rural area (>20 km from large pollution sources)	Barcelona, Urban Background site located on the terrace of a two storey building at 150 m of one of the main avenues of the city	Waldhof, Rural Background site located in the biggest north German forest and health environment with very little influence from local anthropogenic sources	Amsterdam, Roadside Site situated on one of the city's main street arteries and associated with approximately 15 000 vehicles per day	Duisburg, Urban Background site located in a residential area, but also within reach of a motorway (to the north), and industrial premises (to the east and south)	Cabauw, Rural Background site situated in an agricultural area in the western part of The Netherlands, 44 km from the North Sea
Site latitude; longitude	45° 48' N; 8° 38' E	41° 23' N; 2° 07' E	52° 31' N; 10° 46' E	52° 22' N; 4° 51' E	51° 25' N; 6° 50' E	51° 18' N; 4° 55' E
Sampling period	20 days, Oct 2013–Nov 2013	39 days, Feb 2014–Apr 2014	40 days, May 2014–Jul 2014	40 days, Jun 2014–Jul 2014	39 days, Feb 2014–Apr 2014	20 days, Sep 2014–Nov 2014

provided by the site operators and the fractional area of the sampled part of the filter. Fig. 1 to 6 show the concentrations measured for each ion and each site during the field evaluation work. Missing data in these figures generally resulted from sampler breakdown, non-valid sampling or damage to filters apparent after sampling.

3. Uncertainty estimation from the field trial process

The results from each sampled filter analysed by the 6 laboratories were statistically evaluated to calculate the uncertainty in a single measured result. The uncertainty analysis was performed on the whole dataset and on subsets of the data divided up by concentration range. The overall uncertainty includes within-laboratory variability, between-laboratory variability and between-sampler variability.

Laboratory blanks, which were filters taken from a filter box without being transported to site, were analysed to determine detection limits for each ion. Field blanks, taken to site but not exposed, were also analysed as a quality control measure for the field samples. For the purpose of the data analysis described below, the data were divided into three datasets as follows:

(1) Dataset 1 relates to those sites for which a single sampler was used. The sampler used at a particular site may be the same as that used at a different site or it may be different from the samplers used at all other sites. The data set is used to investigate between- and within-laboratory effects and to quantify those effects.

(2) Dataset 2 relates to those sites for which two samplers were used. As for dataset 1, a sampler used at a particular site may be the same as that used at a different site, or it may be different from the samplers used at all other sites. The data set is used to investigate a between-sampler effect and to quantify that effect.

(3) Dataset 1 & 2 were combined and split into four concentration ranges to determine uncertainty over the range of concentrations. For this dataset only the within-laboratory and between-laboratory effects were calculated.

The objective of the data analysis was to evaluate the standard uncertainty to be associated with an individual measured value of concentration, which combines the within-laboratory, between-laboratory and between-sampler effects. The methods employed for these calculations are elaborated upon below.

3.1 Calculating between- and within-laboratory variability

Let there be S sites identified by the index i , $i \in \{1, \dots, S\}$ and L laboratories identified by the index: j , $j \in \{1, \dots, L\}$. Suppose measurements are made by all L laboratories at site i on each of the days identified by the index k , $k \in K_i$. The measured values of concentration are then denoted by:

$$x_{ijk}, k \in K_i, j \in \{1, \dots, L\}, i \in \{1, \dots, S\} \quad (1)$$

The data set is balanced in the sense that all laboratories make measurements at all sites. However, the days K_i on which

Table 2 Laboratories' details and analytical techniques used to measure anions and cations on the filter samples

Laboratory	Analytical technique
CNR Institute of Atmospheric Pollution, (Rome, Italy)	IC ^a for all ions
ECN Energy research Centre of the Netherlands (Petten, the Netherlands)	IC for anions, flow injection for NH ₄ ⁺ , ICP-OES ^b for Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺
FMI Finnish Meteorological Institute (Helsinki, Finland)	IC for all ions
ISCIH Public Research Institute (Madrid, Spain)	IC for anions, photometry for NH ₄ ⁺ , AAS ^c for Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺
TNO Netherlands Organisation for Applied Scientific Research (Zeist, the Netherlands)	IC for anions, continuous flow NH ₄ ⁺ , HR-ICP-MS ^d for Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺
UMB Environment Agency Austria (Vienna, Austria)	IC for all ions

^a IC: ion chromatography. ^b ICP-OES: inductively coupled plasma atomic emission spectroscopy. ^c AAS: atomic absorption spectroscopy. ^d HR-ICP-MS: high resolution inductively coupled plasma mass spectroscopy.

measurements are made can be different from one site to another as the sampling periods were not always the same at all sites.

The data processing comprises two stages. In a first stage, the L measured values corresponding to each site and each day are processed to remove outlying values, and normalised to remove effects associated with the factors of site, sampler and time, as described below. In a second stage, an ANalysis Of VAriance (ANOVA) is applied to the resulting data set corresponding to all sites and all days to decide whether a between-laboratory effect exists. If the effect exists, a calculation of the between- and within-laboratory standard deviations is undertaken. If the effect does not exist, a calculation of the within-laboratory standard deviation only is made. In either case, the within-laboratory standard deviation describes the repeatability

standard deviation for the laboratories. Each part of the data processing is described in detail below.

Outlier rejection is applied to the set of measured values x_{ijk} , $j \in \{1, \dots, L\}$, provided by the L laboratories on day k at site i . Outlier rejection is applied separately for the sets of measured values provided on different days and at different sites.

Outlier rejection involves the following steps using a robust approach:

- (1) Remove any measured value that is zero, denoting a missing value;
- (2) For the non-zero measured values, evaluate the modified Z-score defined by:

$$z_{ijk} = \frac{x_{ijk} - \text{med}(\{x_{ijk}\})}{1.483 \times \text{mad}(\{x_{ijk}\})} \quad (2)$$

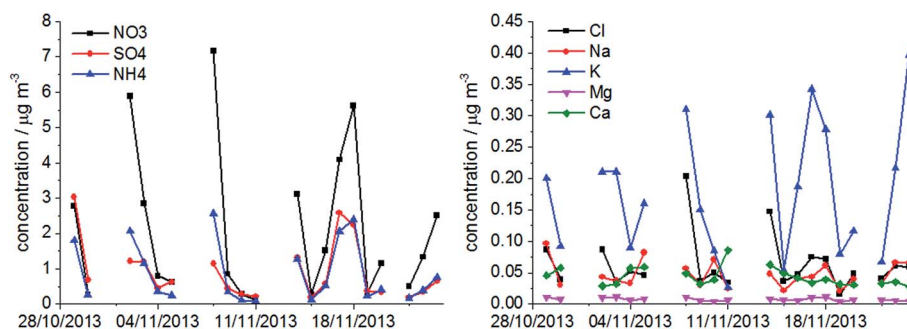


Fig. 1 Ion concentrations measured daily during the trial in Ispra (Italy).

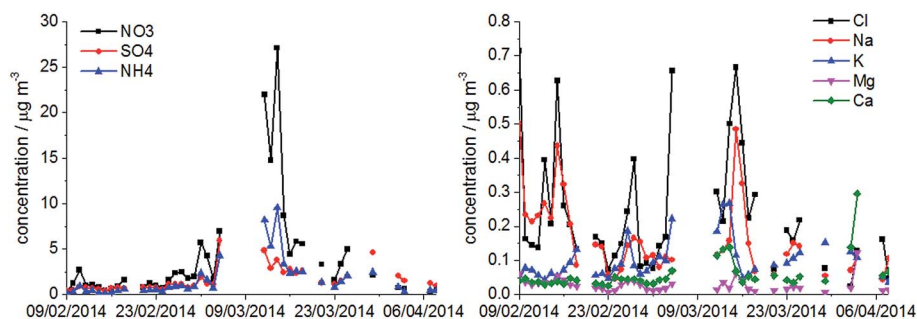


Fig. 2 Ion concentrations measured daily during the trial in Duisburg (Germany).

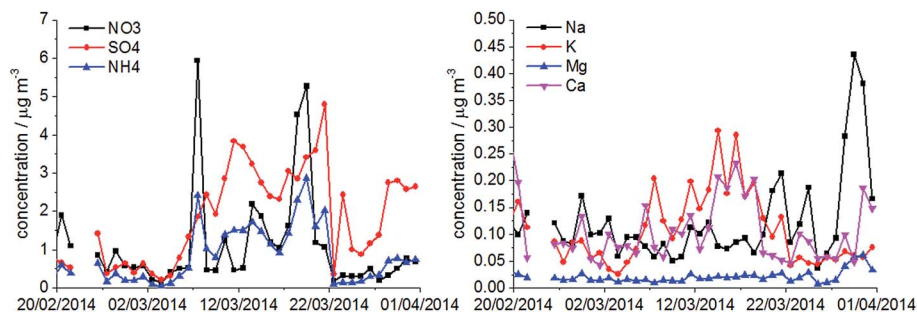


Fig. 3 Ion concentrations measured daily during the trial in Barcelona (Spain).

where: $\text{med}(\{x_{ijk}\}) = \hat{x}_{ijk}$ is the median of the non-zero values $\{x_{ijk} : x_{ijk} \neq 0, j = 1, \dots, L\}$, a robust measure of location, and $\text{mad}(\{x_{ijk}\}) = \text{med}(\{|x_{ijk} - \hat{x}_{ijk}|\})$ is the median-absolute deviation of those values, a robust measure of dispersion;

(3) Remove any measured value for which $|z_{ijk}| > 3.5$.

The procedure for outlier rejection described in steps (2) and (3) follows the recommendation made in Section 1.3.5.17 of the NIST Engineering Statistics Handbook.¹² Outlier rejection can be problematic for small sample sizes, in this case when the number L of laboratories is small. The critical value (of, here, 3.5) for the absolute value of a modified Z-score, which is used to decide whether a measured value is to be considered as an outlier or not, can be adjusted to make outlier rejection easier (using a smaller value of the critical value) or harder (using a larger value). However, such an adjustment leads to a degree of “subjectivity” into the step of outlier rejection, and would need to be clearly justified.

Following outlier rejection, the data for site i and day k is denoted by:

$$x_{ijk}, k \in K_i, j \in J_{ik}, i \in \{1, \dots, S\} \quad (3)$$

where J_{ik} contains the indices of the laboratories for which measured values are retained. Data normalisation involves the following steps:

(1) Evaluate the average

$$\bar{x}_{ik} = \frac{1}{L_{ik}} \sum_{j \in J_{ik}} x_{ijk} \quad (4)$$

where L_{ik} is the number of indices in J_{ik} ;

(2) Shift the measured values by the average \bar{x}_{ik} , and scale the shifted values by \bar{x}_{ik} to obtain normalised values

$$v_{ijk} = \frac{x_{ijk} - \bar{x}_{ik}}{\bar{x}_{ik}}, \quad j \in J_{ik} \quad (5)$$

The average value calculated in step (1) is taken as a reference or consensus value for the concentration of ionic species at the specific site i on the specific day k . The aim of shifting the measured values is to remove, at least approximately, any dependence of measured concentration on the time of measurement, the site at which the measurement is made, and the sampler that is used to make the measurement. The aim of scaling the shifted values is to remove, at least approximately, any dependence of the variability of measured concentration on the value of concentration. The application of scaling is based on the assumption that the repeatability standard deviation is proportional to the measured concentration, *i.e.*, the relative repeatability standard deviation is approximately constant. The normalised data is reported as a fraction (or percentage) of the reference value. Following outlier rejection and data normalisation, the data is denoted by:

$$v_{ijk}, k \in K_i, j \in J_{ik}, i \in \{1, \dots, S\} \quad (6)$$

Since there is no mathematical interest in the factors of site and time, an equivalent representation of the data is as

$$y_{lr}, r \in \{1, \dots, R_l\}, l \in \{1, \dots, L\} \quad (7)$$

which groups the measured values by laboratory. Here, R_l is the number of retained measured values for laboratory l over all

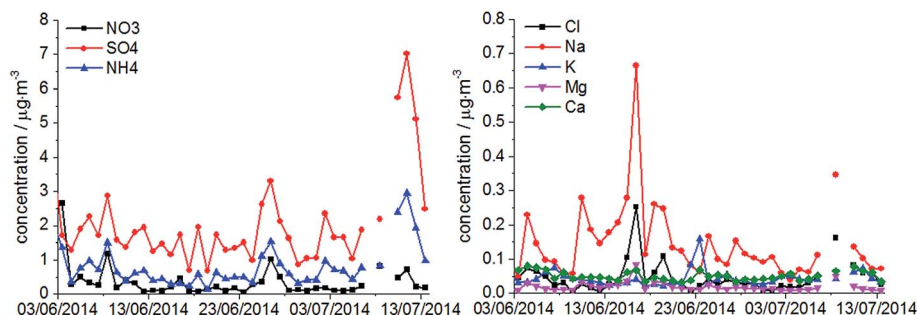


Fig. 4 Ion concentrations measured daily during the trial in Amsterdam (the Netherlands).

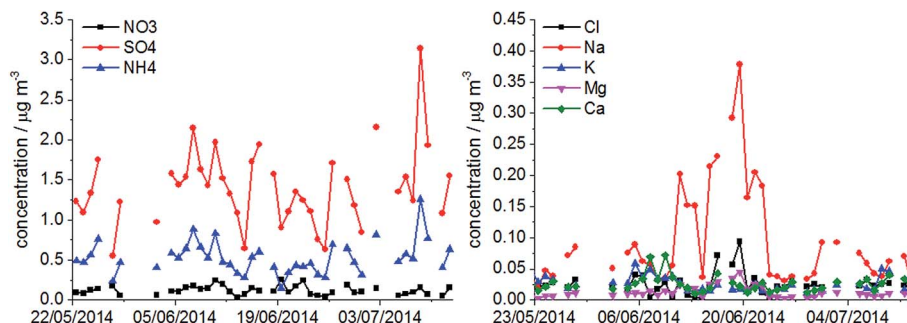


Fig. 5 Ion concentrations measured daily during the trial in Waldhof (Germany).

sites and days, and each y_{lr} equates to one of the normalised values v_{ijk} .

An ANOVA is used to test the null hypothesis that the averages for the laboratories are equal, *i.e.*, there is no laboratory effect. The ANOVA calculation must account for the fact that the data set may be unbalanced, because the numbers of measured values can be different from one laboratory to another. The function “*anovan*”, which is provided in Matlab’s Statistics Toolbox, can be used to perform a (multiway) ANOVA and allows for an unbalanced data set. The function returns a p value that is compared with a critical value p_c , usually 0.01 or 0.05, chosen before the analysis. If $p \geq p_c$, the null hypothesis of no laboratory effect is accepted at a $100p_c\%$ level of confidence. Otherwise, the null hypothesis is rejected at that level of confidence.

The within-laboratory variance (squared standard deviation) is calculated as the pooled variance s^2 of the laboratory values, and is given by:

$$s^2 = \frac{1}{\left(\sum_{l=1}^L R_l\right) - L} \sum_{l=1}^L (R_l - 1) s_l^2 \quad (8)$$

where

$$s_l^2 = \frac{1}{R_l - 1} \sum_{r=1}^{R_l} (y_{lr} - \bar{y}_l)^2 \quad \text{and where } \bar{y}_l = \frac{1}{R_l} \sum_{r=1}^{R_l} y_{lr} \quad (9)$$

If the ANOVA indicates the existence of a between-laboratory effect, then that effect is quantified by the standard deviation s_{lab} of the averages calculated for the laboratories, *i.e.*,

$$s_{\text{lab}}^2 = \frac{1}{L - 1} \sum_{l=1}^L (\bar{y}_l - \bar{\bar{y}})^2 \quad (10)$$

where

$$\bar{\bar{y}} = \frac{1}{L} \sum_{l=1}^L \bar{y}_l \quad (11)$$

In the case that the null hypothesis of no laboratory effect is accepted, the between-laboratory standard deviation is taken to be zero.

3.2 Calculating between-sampler variability

Let there be S sites identified by the index i , $i \in \{1, \dots, S\}$, and L laboratories identified by the index j , $j \in \{1, \dots, L\}$. Suppose measurements are made by all L laboratories at site i on each of the days identified by the index k , $k \in K_i$, using samplers identified by the index f , $f \in F_i$. The measured values of concentration are then denoted by:

$$x_{ijkf}, f \in F_i, k \in K_i, j \in \{1, \dots, L\}, i \in \{1, \dots, S\} \quad (12)$$

The data set is balanced in the sense that all laboratories made measurements at all sites. However, the days K_i on which measurements are made, as well as the samplers F_i used, can be different from one site to another.

In a similar way to that for data set 1, the data processing comprises two stages. In a first stage, considering the data for each sampler separately, the measured values corresponding to

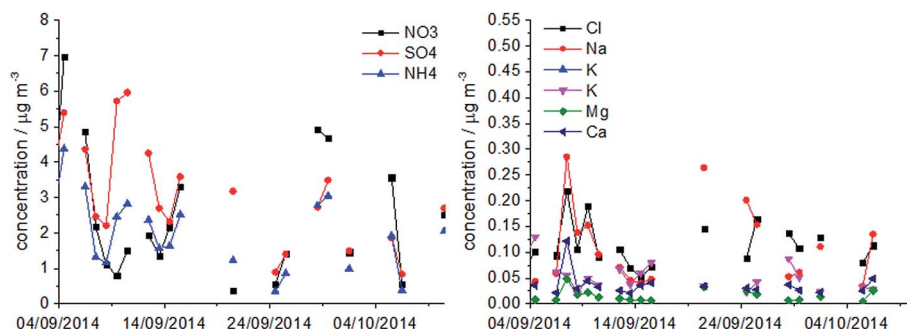


Fig. 6 Ion concentrations measured daily during the trial in Cabauw (the Netherlands).

each site and each day are processed to remove outlying values. Then, considering the data for the samplers together, the values corresponding to each site and each day are normalised to remove effects associated with the factors of site and time, but preserving any sampler effect. In a second stage, an ANOVA is applied to the resulting data set corresponding to all sites, all days and all laboratories to decide whether a between-sampler effect exists. If the effect exists, a calculation of the between-sampler standard deviations is undertaken. Following outlier rejection and data normalisation, the data is denoted by:

$$v_{ijkf}, f \in F_i, k \in K_i, j \in J_{ikf}, i \in \{1, \dots, S\} \quad (13)$$

where J_{ikf} contains the indices of the laboratories for which measured values are retained for site i , day k and sampler f . Since there is no mathematical interest in the factors of site, time and laboratory, an equivalent representation of the data is as:

$$y_{fr}, r \in \{1, \dots, R_f\}, f \in F_1 \cup \dots \cup F_S \quad (14)$$

which groups the measured values by sampler. Here, R_f is the number of retained measured values for sampler f over all sites, days and laboratories, and each y_{fr} equates to one of the normalised values v_{ijkf} . As for data set 1, the data set is generally unbalanced, because the numbers of measured values can be different from one sampler to another.

If an ANOVA indicates the existence of a between-sampler effect, then that effect is quantified by the standard deviation s_{sam} of the averages calculated for the samplers, *i.e.*,

$$s_{\text{sam}}^2 = \frac{1}{F-1} \sum_{f=1}^F (\bar{y}_f - \bar{y})^2 \quad (15)$$

where

$$\bar{y}_f = \frac{1}{R_f} \sum_{r=1}^{R_f} y_{fr}, \quad \bar{y} = \frac{1}{F} \sum_{f=1}^F \bar{y}_f \quad (16)$$

and F is the total number of samplers. In the case that the null hypothesis of no sampler effect is accepted, the between-sampler standard deviation is taken to be zero.

3.3 Combined standard uncertainty

The combined relative standard uncertainty u_{rel} associated with an individual measured value of concentration is given by:

$$u_{\text{rel}}^2 = s^2 + s_{\text{lab}}^2 + s_{\text{sam}}^2 \quad (17)$$

which combines the standard deviations related to respectively within-laboratory, between-laboratory and between-sampler effects. The data analysis described, including the use of ANOVA and the calculations of the standard deviations to quantify the various effects, depends on assumptions about the homogeneity of these effects for different concentrations, sites, laboratories, samplers and time. Graphical displays of the data, in which the data is plotted against these factors, can be useful to identify obvious departures from these assumptions. In cases

that the assumptions do not hold, the results of the data analysis may not be reliable expressions of the various effects considered.

4. Results and discussion

4.1 Data set 1 – between-laboratory and within-laboratory variability

The analysis of variance described above produces p values to assess the between-laboratory effects. If $p \geq p_c$, the null hypothesis of no laboratory effect is accepted at a $100p_c\%$ level of confidence. Otherwise, the null hypothesis is rejected at that level of confidence. p_c can be chosen to be 0.01 (highly significant) or 0.05 (significant). The results show a highly significant between-laboratory effect for all the ions measured. In all cases the between-laboratory variability was calculated and included in the overall uncertainty calculations.

Between-laboratory variability and within-laboratory variability were calculated for all the eight ions. The overall variability was calculated using the 'sum of squares method' to give a combined variability. The results are shown in Table 3 and are equivalent to a standard uncertainty (1σ).

4.2 Dataset 2 – between-sampler variability

Table 4 summarises the results of the between-sampler variability. This method was applied on those results from the site where two samplers were running in parallel. If $p \geq p_c$ the null hypothesis of no between-sampler effect is accepted at a $100p_c\%$ level of confidence.

It can be seen that there is a highly significant between-sampler effect for the NH_4^+ ion, while there is a possibly significant between-sampler effect for the Cl^- ion. However, in both cases the between-sampler variability is small compared to the combined between-laboratory and within-laboratory variability. It is also highly unlikely that a sampler would sample particulate containing these ions differently compared to particulate containing other ions, unless the particulate sample diameter is close to that of the size selective inlet, which is not expected to be the case here. Hence the observation that there is no significant between-sampler variability for six of the eight ions gives us confidence that there is no overall systematic, significant between-sampler effect. For this reason an uncertainty component for between-sampler variability was not

Table 3 Combined variability for all ions on dataset 1

Ion	Between-laboratory variability, %	Within-laboratory variability, %	Combined variability, %
Cl^-	21	27	34
NO_3^-	4.1	7.1	8.2
SO_4^{2-}	3.0	5.1	5.9
Na^+	11	11	16
NH_4^+	4.8	6	7.7
K^+	16	16	22
Mg^{2+}	11	17	20
Ca^{2+}	22	26	34

Table 4 Calculated p values for dataset 2

Ion	p	Significant between-sampler effect	Between-sampler variability, %
Cl ⁻	0.0221	Possible, 2% level	10
NO ₃ ⁻	0.5553	No	1.1
SO ₄ ²⁻	0.2667	No	1.1
Na ⁺	0.3475	No	3.8
NH ₄ ⁺	0.0004	Yes	4.1
K ⁺	0.0484	No	3.2
Mg ²⁺	0.0587	No	6.8
Ca ²⁺	0.7980	No	2.2

included in the calculation of the uncertainty of a single measured result. (The observed differences for NH₄⁺ and Cl⁻ are most likely from some other experimental or analytical effect which has manifested itself as an apparent between-sampler effect although still much smaller than the between-laboratory and within-laboratory variability.)

4.3 Data set 3 – uncertainty over the measured concentration range

Results for each ion from the complete data set were ordered by concentration and then split into four concentration bins with an equal number of measurements in each. The combined expanded uncertainty (2σ , 95% confidence) due to between-laboratory variability and within-laboratory variability were calculated for each concentration bin, the results of which are

shown in Fig. 7. In Table 5 the maximum, minimum and median of the concentration ranges are reported as well as the combined uncertainties. The charts have all been plotted with the same y-axis scale to aid comparison of the uncertainty associated with the measurement of different ions.

The uncertainty for all ions is generally consistent across the Q2 to Q4 concentration range, with a larger uncertainty for the Q1 concentration demonstration the expected characteristic empirical concentration-dependent uncertainty function of analytical measurement of the form: $\sigma = \sqrt{\alpha^2 + (\beta c)^2}$ where σ represents uncertainty, c is concentration and α and β are constants. The uncertainty for the Q1 concentrations becomes limited by the detection limit. For the Q2 to Q4 range the uncertainty of a single measurement result for all ions is $\leq 30\%$ (2σ , 95% confidence) except Cl⁻ and Ca²⁺ where this is $\leq 35\%$ (2σ , 95% confidence). These results are very similar to those found in previous studies.¹³

4.4 Capabilities of the method

An expanded combined uncertainty was calculated for the two rural background sites, which represent the locations where measurements should be taken according to the European Directive. The data per site were treated as dataset 1 described above but the index i fixed. The results are shown in Fig. 8 and report uncertainty for each ion calculated on the whole dataset per site, rather than being ranked by concentration. Much higher uncertainties were found in this case, especially for the

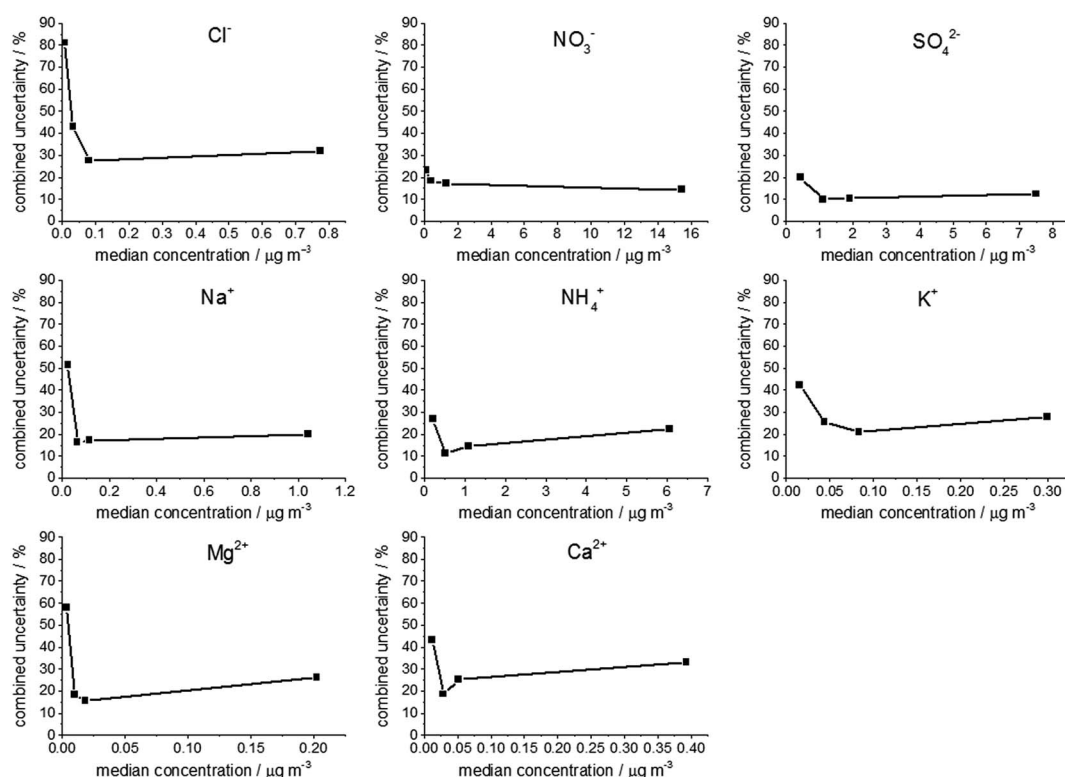
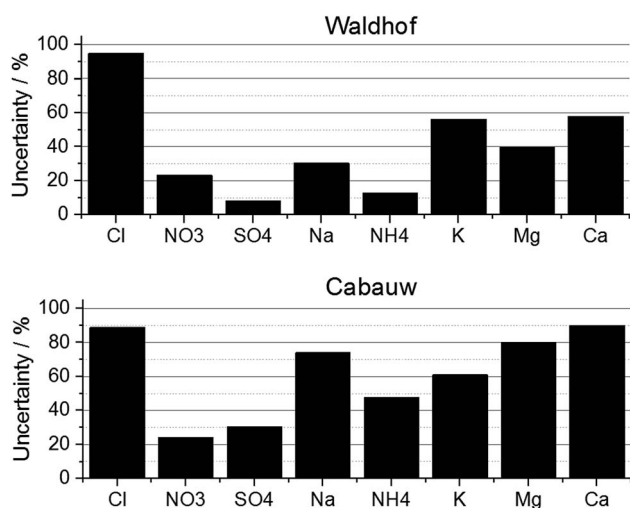


Fig. 7 Combined uncertainty at 95% confidence level for each ion and each concentration range. The x-axis reports the median of each concentration range.

Table 5 Between-laboratory variability, inter-laboratory variability, combined uncertainty at 95% level of confidence, minimum and maximum ambient concentrations for each concentration range for each ion

Component	Concentration quartile	Between-laboratory variability, %	Within-laboratory variability, %	Expanded combined uncertainty, %	Minimum, $\mu\text{g m}^{-3}$	Maximum, $\mu\text{g m}^{-3}$	Median, $\mu\text{g m}^{-3}$
Cl^-	Q1	56	59	81	0.0005	0.014	0.0072
Cl^-	Q2	27	34	43	0.014	0.052	0.033
Cl^-	Q3	12	25	28	0.052	0.11	0.081
Cl^-	Q4	5.9	32	32	0.110	1.4	0.78
NO_3^-	Q1	16	17	23	0.0017	0.20	0.10
NO_3^-	Q2	6.1	17	18	0.20	0.63	0.42
NO_3^-	Q3	7.3	16	17	0.63	2.0	1.3
NO_3^-	Q4	5.0	13	14	2.0	29	15
SO_4^{2-}	Q1	7.7	18	20	0.051	0.80	0.42
SO_4^{2-}	Q2	3.8	9.2	10	0.80	1.4	1.1
SO_4^{2-}	Q3	6.5	8.2	10	1.4	2.4	1.9
SO_4^{2-}	Q4	4.2	12	12	2.4	13	7.5
Na^+	Q1	33	40	52	0.0026	0.045	0.024
Na^+	Q2	6.9	15	17	0.045	0.083	0.064
Na^+	Q3	5.9	16	17	0.083	0.15	0.12
Na^+	Q4	11	17	20	0.146	1.9	1.0
NH_4^+	Q1	12	24	27	0.040	0.38	0.21
NH_4^+	Q2	5.9	9.5	11	0.38	0.67	0.52
NH_4^+	Q3	8.2	12	15	0.67	1.5	1.1
NH_4^+	Q4	16	16	22	1.5	11	6.1
K^+	Q1	32	27	42	0.0033	0.028	0.016
K^+	Q2	11	23	26	0.028	0.060	0.044
K^+	Q3	9.6	19	21	0.060	0.11	0.083
K^+	Q4	19	20	28	0.11	0.49	0.30
Mg^{2+}	Q1	28	51	58	0.0005	0.0069	0.0037
Mg^{2+}	Q2	6.3	17	18	0.0069	0.014	0.010
Mg^{2+}	Q3	3.8	15	16	0.014	0.023	0.018
Mg^{2+}	Q4	8.3	25	26	0.023	0.38	0.20
Ca^{2+}	Q1	25	35	43	0.0019	0.021	0.012
Ca^{2+}	Q2	5.7	18	19	0.021	0.036	0.029
Ca^{2+}	Q3	9.8	23	25	0.036	0.067	0.052
Ca^{2+}	Q4	12	31	33	0.067	0.72	0.39

**Fig. 8** Expanded combined uncertainty (at the 95% confidence level) for the two rural background sites in the field campaign. The overall uncertainty can be over 50% for ions like Cl^- , Na^+ , K^+ , Mg^{2+} and Ca^{2+} .

Cabauw site. However, the small number of days of sampling for this site could have contributed to the very high uncertainty for almost all the ions (20 days against 40 days at Waldhof). Overall, the uncertainties for Cl^- , Na^+ , K^+ , Mg^{2+} and Ca^{2+} are estimated to be over 50% at rural sites. This is due to the low concentrations expected from these ions, variability in the reagent blank and filter blank levels, especially for Cl^- in quartz filters, and perhaps also because of solubility issues for some compounds like calcium salts.

4.5 Detection limit

Laboratory blank filters were repeatedly analysed by each laboratory and the results pooled to determine the method detection limit in μg per filter punch and $\mu\text{g m}^{-3}$, for each ion according to the following equation:

$$\text{Detection limit} = \text{SD} \times t_{99, n-1} \quad (18)$$

where: SD = the standard deviation of the repeated measurements, $t_{99, n-1}$ = the student t factor with a level of confidence of 99% for $n - 1$ degrees of freedom, n = the number of repeat measurements.

Table 6 Detection limits for each ion and the average equivalent ambient air concentration for each ion measured on the laboratory blank filters (* indicates an estimated value)

Ion	<i>n</i>	Detection limits	
		µg per filter punch	µg m ⁻³
Cl ⁻	48	0.477	0.01
NO ₃ ⁻	51	1.68	0.03
SO ₄ ²⁻	2	—	0.03*
Na ⁺	57	0.868	0.01
NH ₄ ⁺	73	1.40	0.02
K ⁺	63	0.243	0.001
Mg ²⁺	61	0.085	0.001
Ca ²⁺	68	0.611	0.01

Table 7 Detection limits for each ion and the average equivalent ambient air concentration for each ion measured on the field blank filters

Ion	Detection limit/µg m ⁻³	
	All labs	5 labs
Cl ⁻	0.03	0.01
NO ₃ ⁻	0.02	0.02
SO ₄ ²⁻	0.09	0.07
Na ⁺	0.02	0.01
NH ₄ ⁺	0.02	0.01
K ⁺	0.01	0.005
Mg ²⁺	0.003	0.002
Ca ²⁺	0.02	0.01

One laboratory appeared to have a systematic offset in their laboratory blank data and this data has been excluded from the detection limit calculations. Table 6 gives the calculated method detection limits for each ion and the average equivalent ambient air concentration for each ion measured on the laboratory blank filters.

It should be noted that only two measurements of laboratory blank detected the SO₄²⁻ ion, therefore a detection limit cannot be calculated with great confidence. As all valid detection limits are ≤0.03 µg m⁻³ it can be reasonably assumed that the real method detection limit for SO₄²⁻ can be taken as 0.03 µg m⁻³ since the analytical characteristics vary little between ions.

Field blanks were analysed by each laboratory and the average equivalent ambient air concentration level of each ion is shown in the Table 7 and the results are very similar to the detection limits calculated from the laboratory blanks.

5. Conclusions

The results of the field campaign conducted by CEN/TC 264/WG34 to validate the standard method for the measurements of anions and cations in PM_{2.5} and to assess the overall uncertainty have been presented. The uncertainty in the concentrations was found to be dominated by within- and between-laboratory variability. Any possible between-sampler

effect was considered negligible since the majority of ions did not show any significant between-sampler differences.

The statistical analysis carried out on grouped concentration ranges showed that except at low concentrations, the relative expanded uncertainty (at 95% confidence level) for the overall method is expected to be below 30% for all ions but Cl⁻ and Ca²⁺. The European Directive requires measurements of ions in PM_{2.5} in rural locations but it does not specify a limit value for the uncertainty. By using the data from rural background sites in this trial it had been shown that the expanded uncertainty at such locations can be as high as 90% for Cl⁻ and generally over 50% for other ions. Lower expanded uncertainty at rural sites were found for NO₃⁻, SO₄²⁻ and NH₄⁺ which are less effected by blank level variability and any solubility issues. The general expanded uncertainty decreases for higher concentrations. The limit of detection was also calculated for all ions and it was found to be 0.03 µg m⁻³ or below and was consistent with previous studies.¹⁴

It is hoped that the detail provided in this paper will give clarity and confidence in the underpinning science for future users of the standard method and will also provide a detailed framework for assessing the uncertainty and method performance characteristics for future field trials of this type. This study has also highlighted the uncertainty with which data can be obtained using this method and therefore by corollary imposes a limitation of the level certainty with which conclusions about trends in concentration and comparability of concentrations between locations can be made.

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