# Development of a detailed measurement model for the assessment of atmospheric aerosols water soluble fraction by Ion Chromatography

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## Introduction

Air composition is known to have a relevant impact on public health, on the environment and on meteorology and climate. The chemical characterization of air gaseous and aerosol fraction is used to monitor risks from exposition to polluted air and to develop air transport and climate models. Air is appropriately sampled, and aerosols are collected in conveniently chosen filters, kept and treated according to the planned strategy. The ionic composition of the water soluble fraction of aerosols, assessed by Ion Chromatography, IC, is particularly useful to estimate the mineral composition of aerosols of both natural and anthropogenic origins .
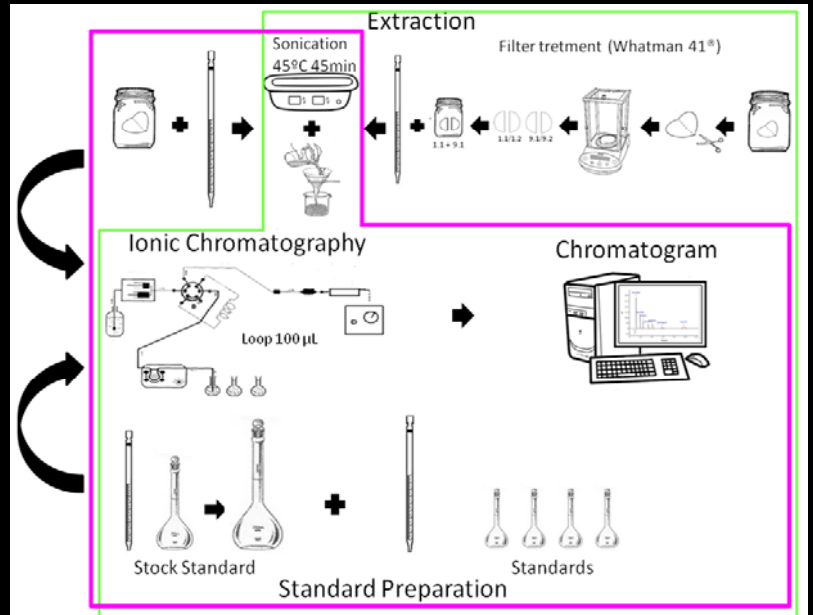
The reliability of conclusions about the systems under study depends on the quality of the measurement results.

The assessment of trends in air composition must be supported on measurement results traced to a common reference and reported with measurement uncertainty.
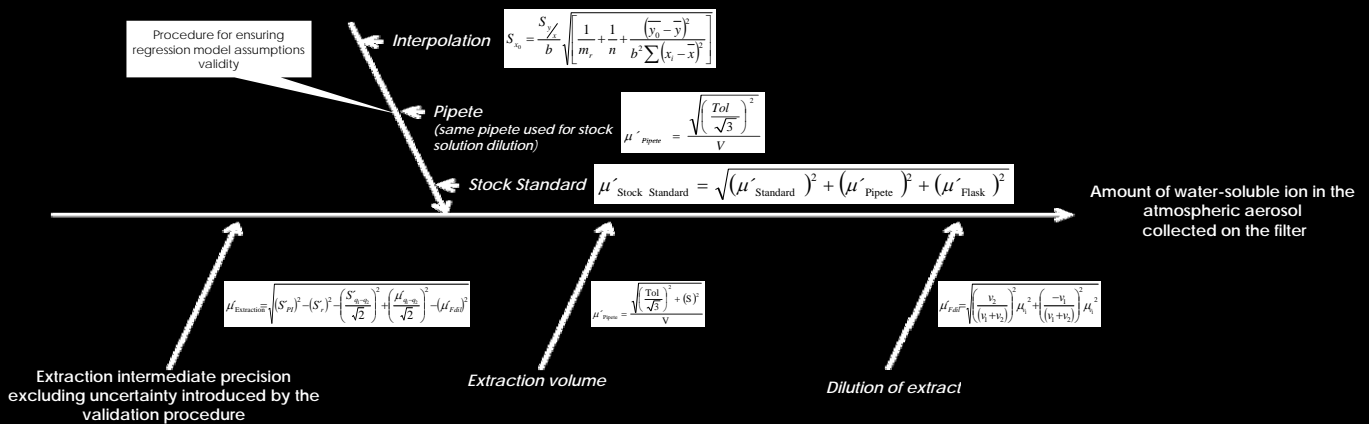
In this work, a metrological model has been developed for the determination of ion composition of the atmospheric aerosols water soluble fraction according to an operationally defined measurement procedure. The uncertainty associated with the results is evaluated by the Differential Approach. The metrological relevance of individual analytical steps and effects has been identified. The uncertainty budget is divided in the extraction, extract dilution and ionic chromatography quantification components.

The evaluation of the extraction step involved the estimation of the intermediate precision from duplicate analysis of pooled urban aerosol samples prepared from real samples to ensure homogeneity. The uncertainty associated with the preparation of duplicate filters was considered.

## Measurement Procedure & Precision validation procedure



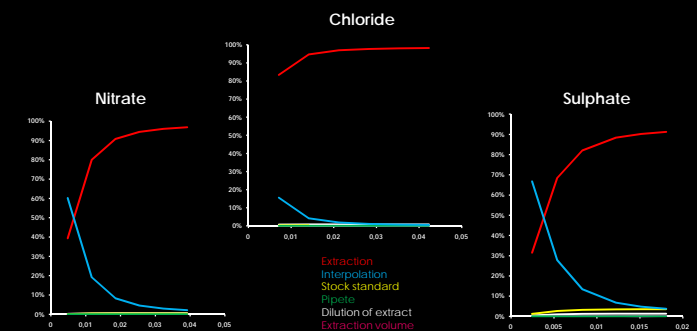## Indentification and Quantification of uncertainty parameters



Procedure for ensuring regression model assumptions validity

*Interpolation*

$$S_{x_0} = \frac{S_{y/x}}{b}\sqrt{\frac{1}{m_r}+\frac{1}{n}+\frac{(\overline{y_0}-\overline{y})^2}{b^2\sum(x_i-\overline{x})^2}}$$

*Pipete* (same pipete used for stock solution dilution)

$$\mu'_{Pipete} = \frac{\sqrt{\left(\frac{Tol}{\sqrt{3}}\right)^2}}{V}$$

*Stock Standard*

$$\mu'_{Stock\ Standard} = \sqrt{(\mu'_{Standard})^2+(\mu'_{Pipete})^2+(\mu'_{Flask})^2}$$

Amount of water-soluble ion in the atmospheric aerosol collected on the filter

$$\mu_{Extraction}=\sqrt{(S_{PI})^2-(S'_r)^2-\left(\frac{S'_{q_i-q_i}}{\sqrt{2}}\right)^2+\left(\frac{\mu'_{q_i-q_i}}{\sqrt{2}}\right)^2-(\mu'_{Fdil})^2}$$

Extraction intermediate precision excluding uncertainty introduced by the validation procedure

$$\mu'_{Pipete}=\frac{\sqrt{\left(\frac{Tol}{\sqrt{3}}\right)^2+(S)^2}}{V}$$

Extraction volume

$$\mu_{Fdil}=\sqrt{\left(\frac{v_2}{(v_1+v_2)}\right)^2{\mu_i}^2+\left(\frac{-v_1}{(v_1+v_2)}\right)^2{\mu_i}^2}$$

Dilution of extract

## Results

### Variation of the relative expanded uncertainty with anion content



### Variation of the percentage contribution of the uncertainty components with the sample content
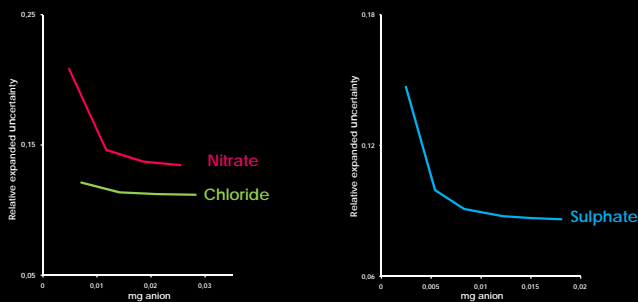


The relative expanded uncertainty decreases with the increase of the mass of ion in the filter. This trend is not so strong for chloride due to the smaller contribution of the interpolation uncertainty component. The relative interpolation uncertainty varies significantly with the anion concentration. The relative expanded uncertainty is fit for the intended use since is smaller than a target value of 20%.

For the determination of water extractable nitrate and sulphate, in defined conditions, from aerosols collected in filters, the contribution of the statistical interpolation of the sample signal in the calibration curve is major at the lower fraction of the studied analytical range and minor for higher sample contents. The linear unweighted regression model was used after a detailed validation of model assumptions for calibration standards quality, and homosedasticity and linearity of the instrumental response. For higher samples contents or the all analytical range for chloride, the uncertainty associated with the intermediate precision of the extraction clearly dominates the uncertainty budget. This component was estimated after subtracting the uncertainty introduced by the validation procedure of the extraction precision. The other uncertainty components are minor ones and resources in managing these components can be saved with no relevant impact on measurements quality.