

INTERCOMPARISON AEROSOL CHEMICAL SPECIATION MONITORS (ACSM): CALIBRATION PROTOCOLS AND INSTRUMENT PERFORMANCE EVALUATIONS

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RESUME

Ce travail décrit les résultats obtenus lors de l'exercice d'intercomparaison 2016 des moniteurs de spéciation chimique des aérosols (ACSM) réalisé au Centre de calibrage des moniteurs chimiques des aérosols (ACMCC, France). Quinze ACSM quadripolaires (Q_ACSM) du réseau de l'Infrastructure européenne de recherche pour l'observation des aérosols, des nuages et des gaz à l'état de traces (ACTRIS) ont été étalonnés à l'aide d'une nouvelle procédure qui permet d'acquérir des données d'étalonnage dans les mêmes conditions de fonctionnement que celles utilisées lors de l'échantillonnage et donc d'obtenir des informations représentatives des performances des instruments. La nouvelle procédure d'étalonnage a notamment permis de réduire la dispersion des concentrations massiques de sulfate mesurées, améliorant ainsi la reproductibilité des mesures des espèces inorganiques entre les ACSM ainsi que la cohérence avec les instruments indépendants situés au même endroit. Les procédures d'étalonnage testées ont également permis d'étudier les artefacts des instruments individuels, tels que la surestimation du m/z 44 de l'aérosol organique. Cet effet a été quantifié par le rapport m/z (masse sur charge) 44 sur nitrate mesuré pendant les étalonnages du nitrate d'ammonium, avec des valeurs allant de 0,03 à 0,26, montrant qu'il peut être significatif pour certains instruments. La correction de la table de fragmentation proposée précédemment pour tenir compte de cet artefact a été appliquée aux mesures acquises au cours de cette étude. Pour certains instruments (ceux présentant des artefacts élevés), cette correction de la table de fragmentation a conduit à une " surcorrection " du signal f44 (m/z 44/Org). Cette correction, basée sur des mesures effectuées avec du NH₄NO₃ pur, suppose que l'ampleur de l'artefact est indépendante de la composition chimique. En utilisant des données acquises à différents rapports de mélange de NH₄NO₃ (à partir de solutions de NH₄NO₃ et de (NH₄)₂SO₄), nous observons que l'ampleur de l'artefact varie en fonction de la composition. Nous avons appliqué ici une correction actualisée, dépendant de la fraction massique de NO₃ ambiante, qui a permis d'améliorer la concordance du signal organique entre les instruments. Ce travail illustre les avantages de l'intégration de nouvelles procédures d'étalonnage et de corrections d'artefacts, mais souligne également les avantages de ces exercices d'intercomparaison pour continuer à améliorer notre connaissance du fonctionnement de ces instruments, et nous aider à interpréter la chimie atmosphérique.

ABSTRACT

This work describes results obtained from the 2016 Aerosol Chemical Speciation Monitor (ACSM) intercomparison exercise performed at the Aerosol Chemical Monitor Calibration Center (ACMCC, France). Fifteen quadrupole ACSMs (Q_ACSM) from the European Research Infrastructure for the observation of Aerosols, Clouds and Trace gases (ACTRIS) network were calibrated using a new procedure that acquires calibration data under the same operating conditions as those used during sampling and hence gets information representative of instrument performance. The new calibration procedure notably resulted in a decrease in the spread of the measured sulfate mass concentrations, improving the reproducibility of inorganic species measurements between ACSMs as well as the consistency with co-located independent instruments. Tested calibration procedures also allowed for the investigation of artifacts in individual instruments, such as the overestimation of m/z 44 from organic aerosol. This effect was quantified by the m/z (mass-to-charge) 44 to nitrate ratio measured during ammonium nitrate calibrations, with values ranging from 0.03 to 0.26, showing that it can be significant for some instruments. The fragmentation table correction previously proposed to account for this artifact was

applied to the measurements acquired during this study. For some instruments (those with high artifacts), this fragmentation table adjustment led to an “overcorrection” of the f44 (m/z 44/Org) signal. This correction based on measurements made with pure NH_4NO_3 , assumes that the magnitude of the artifact is independent of chemical composition. Using data acquired at different NH_4NO_3 mixing ratios (from solutions of NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$) we observe that the magnitude of the artifact varies as a function of composition. Here we applied an updated correction, dependent on the ambient NO_3 mass fraction, which resulted in an improved agreement in organic signal among instruments. This work illustrates the benefits of integrating new calibration procedures and artifact corrections, but also highlights the benefits of these intercomparison exercises to continue to improve our knowledge of how these instruments operate, and assist us in interpreting atmospheric chemistry.

MOTS-CLÉS : Chimie d'aérosols, métrologie, ACTRIS / **KEYWORDS**: Aerosol chemistry, Calibration, Intercomparison, ACTRIS

1. INTRODUCTION

Continuous and long-term measurements of essential climatologically relevant parameters, such as aerosol chemistry and physical properties, are critical to resolve aerosol-cloud-climate interactions and to gain insights into the role they play in climate change and air quality. Recently in Europe, significant efforts have contributed to the installation and maintenance of a number of different observation stations in a range of differing environments (Frohlich et al. 2015a). These stations notably belong to the European Research Infrastructure for the observation of Aerosol, Clouds, and Trace Gases (ACTRIS, www.actris.eu). The physical and chemical properties of aerosols are measured at a number of stations. Up until recently, aerosol chemistry was acquired through offline filter measurements, or over short periods using more advanced techniques such as aerosol mass spectrometry (Canagaratna et al. 2007). Development of the Aerosol Chemical Speciation Monitor (ACSM) allows near-autonomous continuous measurements of aerosol chemistry, with minimal intervention from the user. The ACSM uses either a quadrupole mass spectrometer (Q-ACSM) or a time of flight mass spectrometer (ToF-ACSM) (Frohlich et al. 2015) to measure particle composition. This instrument designed specifically for in-situ measurements of non-refractory submicron (NR-PM₁) aerosol species has a time resolution of approximately 15 to 30 min. It is based on aerosol mass spectrometry (AMS) technology and has demonstrated its suitability for continuous monitoring over the last eight years.

Aerosol chemistry measurements are being increasingly used to constrain predictive models to forecast atmospheric processes and evolution (e.g., Ciarelli et al. 2017), and therefore it is imperative to ensure high quality data to develop and evaluate these models. To satisfy this need, a number of calibration centers have been created in Europe with the specific objective to identify measurement guidelines and calibration procedures. The Aerosol Chemical Monitor Calibration Center (ACMCC) is part of the European Center for Aerosol Calibration (ECAC, www.actris-ecac.eu), and is oriented towards the calibration of online aerosol chemistry measurements (Crenn et al. 2015). It notably aims to calibrate and intercompare ACSM instruments used at ACTRIS stations at least every three years, so to ensure the continuity of long-term quality assured data within this research infrastructure. The first ACSM intercomparison took place at the ACMCC in December 2013. This work describes results from a second intercomparison exercise, held in March 2016, at the ACMCC. This intercomparison specifically addressed new recommended calibration procedures, and evaluated recently proposed corrections for artifacts related to the organic aerosol measurements.

2. METHODOLOGY

A total of 15 Q-ACSM instruments were installed at the Site Instrumental de Recherche par Teledetection Atmosphérique (SIRTA) station during the month of March 2016. The SIRTA station is an ACTRIS national facility for aerosol, cloud, and gas-phase measurements and is located 20 km south of Paris, in Gif-sur-Yvette. A number of instruments were operated alongside the Q-ACSM instruments at the SIRTA site. These instruments included the Fine Dust Aerosol Spectrometer (FIDAS, PALAS), providing size-segregated particle mass concentrations every 15 min over a total of 64 size bins ranging from 180 nm up to 18,000 nm. A tapering element oscillating microbalance equipped with filter dynamic measurement system (TEOMFDMS, Ecomasure) provided total particle mass concentration of the PM₁ component.

3. RESULTS AND DISCUSSION

This work presents calibrations performed with the same sampling protocol as during ambient sampling, ensuring that data is acquired and analyzed under the same operating conditions used during measurements. Results showed that the use of full-scan mode calibration data (as opposed to jump-scan mode data) improved the comparison of different chemical mass loading (specifically SO_4) with external data and improved the correlation of the measured mass concentrations among the 15 instruments (Figure 1). Based on these results,

a new set of calibration protocols are recommended by the manufacturer as well as within the ACTRIS standard operating procedures. These results illustrate that these online aerosol mass spectrometry instruments have good comparability and are within the $\pm 30\%$ uncertainty range recommended for these instruments. This uncertainty range should always be considered when comparing these instruments to other co-located instruments. These intercomparison exercises illustrates that ACSM data is highly valuable for future atmospheric model evaluation and development. In addition, new calibration procedures have the added advantage of acquiring a full mass spectrum providing each user the opportunity to assess and quantify the presence of instrument artifacts, notably the m/z 44 artifact. Applying the m/z artifact correction following Pieber et al. (2016) increased the variability in both the measured f_{44} and the total organic mass loading. Moreover, in cases of high artifact values (m/z 44/ $\text{NO}_3 > 0.10$) the fragmentation table adjustment as per Pieber et al. (2016), results in sometimes unrealistically low f_{44} values. In ambient air, NO_3 mass fraction (NO_3_MF) may occasionally exceed 0.5 but rarely reaches 0.8. An alternative correction, accounting for varying NO_3_MF , was tested. Application of this alternative correction resulted in significant improvements in the f_{44} reproducibility, as well as for other dominant organic fragments, leading to an improvement in the agreement of the total measured organic mass concentrations over all instruments.

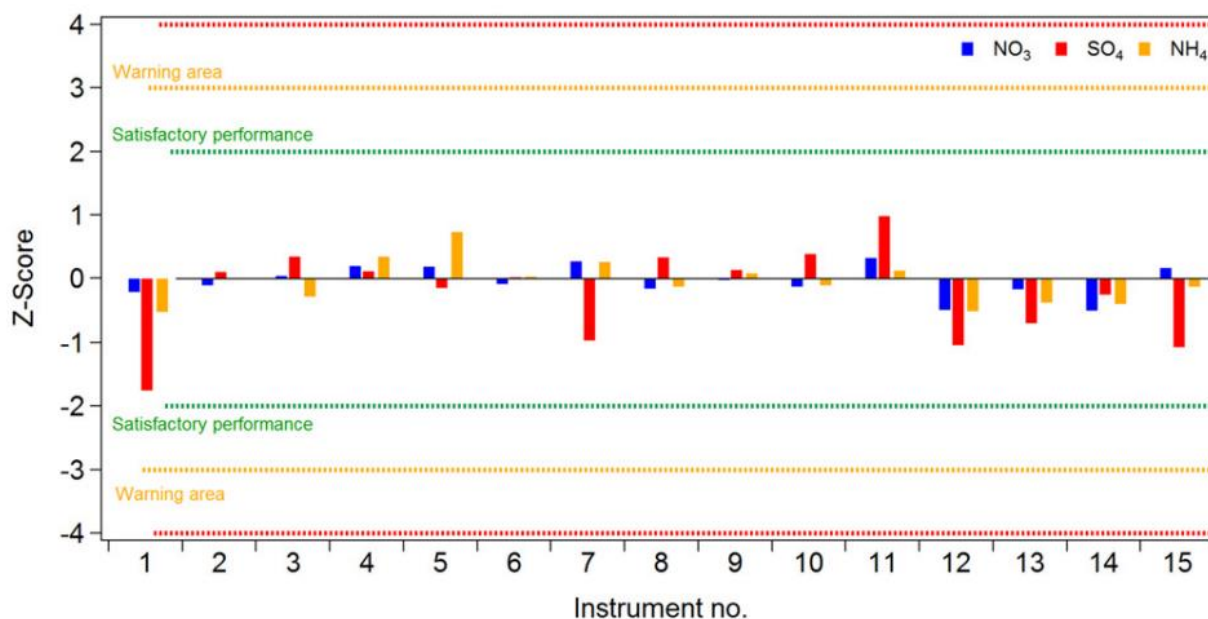


Figure 1. Z-score values calculated for the 15 participating ACSM instruments for inorganic species.

The analysis and interpretation of ACSM data, especially related to the organic spectra, are constantly evolving, as is our knowledge of the instrument response to different chemical species (Hu et al. 2017; Pieber et al. 2016). It is possible that the high fractions of measured nitrate during this intercomparison were in part due to the presence of organic nitrates (Kieudler-Scharr et al. 2016). Given the spatial distribution of ACSM instruments in Europe and the continuous sampling nature of the ACSM measurements, understanding how the instruments respond to different organics species, including organic nitrates, is essential, and will be the focus of future intercomparison exercises.

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