



## ACTRIS 2 (ECAC-ACMCC) Intercomparison of Aerosol Chemical Speciation Monitors, November 2018

**Project No.:** ACSM-2018-1-18

### **Basic information**

**Location of the quality assurance:** SIRTA/ACMCC, LSCE, Lab. 705

**Delivery date:** Before November 13th, 2018

**Setup in the laboratory:** November 13th 2018

**Workshop period:** November 19th to November 23<sup>th</sup>, 2018

| Principal investigator | Institute | Participant   | Instrument |
|------------------------|-----------|---------------|------------|
| Evelyn Freney          | PUY       | Evelyn Freney | ToFACSM013 |

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## Summary

This report summarizes results obtained for the PUY quadrupole Aerosol Chemical Speciation Monitor (QACSM) during the 2018 ACMCC ACTRIS-2 workshop. It is divided into four main sections. The first section describes the instrumental set-up and data treatment methodologies used for the workshop. The second section presents results obtained during the initial intercomparison, where instruments were operated as delivered by participants. The third section describes calibrations and maintenance (if any) performed during the workshop. The last section presents results obtained during a second intercomparison campaign, where instruments were tuned and calibrated at ACMCC.

Performance evaluation includes:

- 1) The instrument performance is within the acceptable limits evaluated using a Z-score analysis, as described by ISO 5725-2.
- 2) The instrument is in overall good agreement - i.e., within  $\pm 30\%$  - with a reference dataset, the latter corresponding to a reference instrument and/or the robust median of intercomparison participants datasets.

The reference dataset is that measured by the SIRTA instrument. This instrument successfully participated in the previous ACSM intercomparisons and didn't travel prior to the workshop (unlike other instruments). It is regularly maintained and calibrated by the ACMCC staff. The robust median refers to the median value of all participating PM1 QACSM and excludes the PM2.5 QACSM instruments.

Based on these tests, the PUY instrument passed the quality standards required as part of the ACTRIS research infrastructure.

### 1. Overview of the instrumental set-up and data treatment methodologies

Instruments were asked to be delivered at ACMCC no later than the 13<sup>th</sup> of November. They were installed and switched on by ACMCC personnel during the week from the 12<sup>th</sup> to the 16<sup>th</sup> of November. There were four different tables, each containing four instruments. Each table had its own inlet, fitted with a common sampling head. All sampling lines were composed of  $\frac{1}{2}$  inch copper tubes and were the same length for each instrument. Each instrument sampled 3 liters from the main inlet line, this flow was controlled by external sample line flow pumps. Instruments were fitted with or without an individual dryer, as used at their usual sampling site and/or as requested by participants.

Instruments were compared with the SIRTA reference instrument and also with the robust median of all instruments through Z-score analysis. For comparison to both of these reference datasets, it is expected that good instrument performance is met when the participant's results fall within a well characterized uncertainty for aerosol mass spectrometers, taken here as  $\pm 30\%$  (Bahreini et al., 2009, Middlebrook et al., 2012; Crenn et al., 2015).

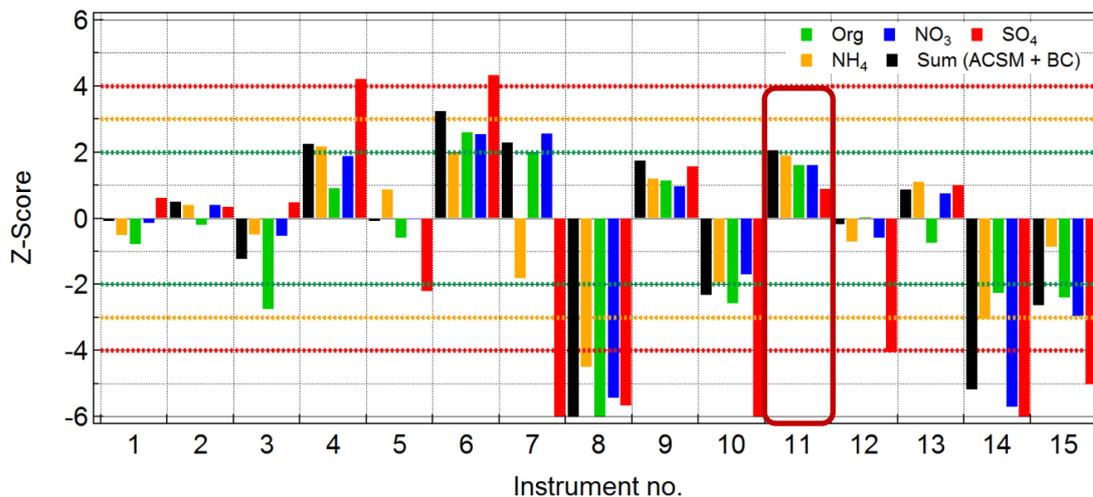
The data treatment methodology used here was validated in the first ACTRIS1 ACSM intercomparison (Crenn et al., 2015). In particular, the Z-score analysis was applied following the standards defined by the international standard organization (ISO). This method has been evaluated according to ISO 5752-2 and provides a means to evaluate instrument performance relative to other instruments participating in the intercomparison. Such a method has been applied within other European intercomparison exercises (JRC technical intercomparison reports). The Z-score tests evaluates if the variations in the different instruments from the reference value fall within a defined criterion, following Eq.1:

$$Z_i = \frac{X_I - X^*}{\sigma^*} \tag{Eq. 1}$$

Where  $X_I$  is the robust median of the selected instruments,  $X^*$  is the value of the instrument being compared and  $\sigma^*$  is the standard deviation of this latter instrument. The robust median target values were determined based on datasets obtained by PM<sub>1</sub> ACSM only (i.e., for consistency, the few PM<sub>2.5</sub> ACSMs were not considered for this target value calculation). According to this test, instrument performance is considered acceptable when values fall between 2 and -2 (indicated by the green lines in Figures 2.1 and 4.3).

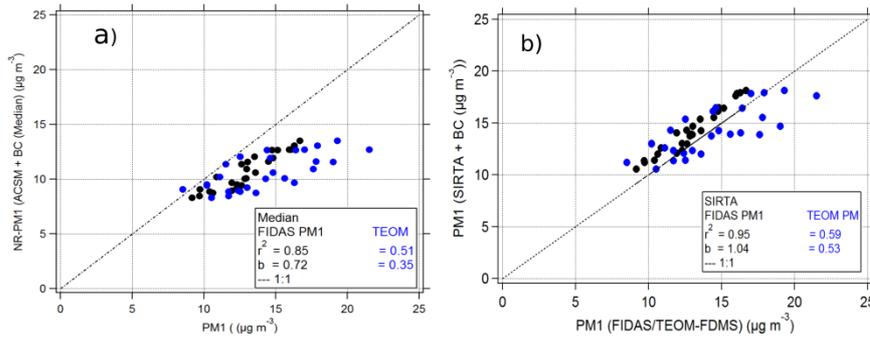
## 2. Results from initial intercomparison campaign

Once installed by ACMCC personnel, instruments were turned on with tunings indicated by participants, and sampled ambient air at the station from the 16<sup>th</sup> to the 19<sup>th</sup> of November 2018 for the initial intercomparison. Fifteen instruments were compared all together during a limited period of 18<sup>th</sup> Nov 18hrs to 19<sup>th</sup> Nov 08 hrs. The Z-score test illustrates the instrument performances during this period, (Figure 2.1) where each instrument was compared to the robust median of the participating instruments.



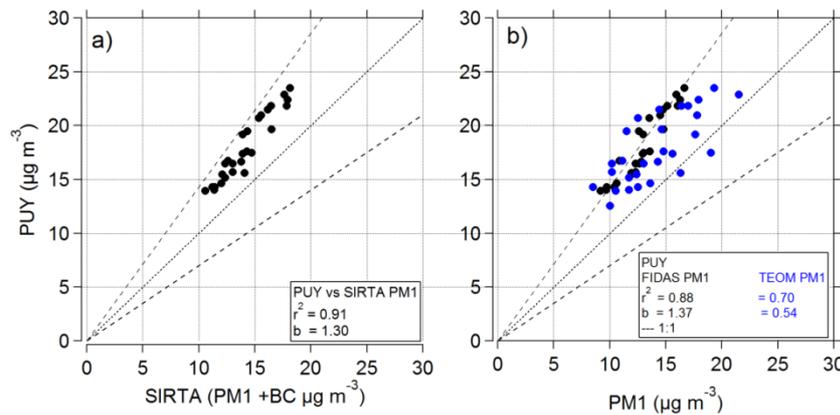
**Figure 2.1. Z-score calculation for each species measured by the ACSM for each instrument that participated in the initial intercomparison campaign (18<sup>th</sup> Nov 18hrs to 19<sup>th</sup> Nov 08 hrs). The red rectangle highlights the PUY instrument.**

The PUY instrument agreed well with median concentrations from the other ACSM instrument, being within the acceptable limits. Given the large variability in instrument performance prior to calibration, the median value is not considered to be representative for comparison, and therefore a second comparison is also made using the SIRTA instrument. This is illustrated in Figure 2.2 below where the median NR-PM<sub>1</sub> + BC mass concentration is compared with the NR-PM<sub>1</sub> mass concentration measured from the Fine Dust Aerosol Spectrometer (FIDAS, Palas ®) and the Tapering Elemental Oscillating Microbalance with Filter Dynamics Measurement System (TEOM-FDMS) instruments, giving a slope of 0.72 and 0.37 respectively. In comparison the NR-PM<sub>1</sub> + BC mass concentration measured from the SIRTA instrument compares considerably better with slope values of 1.08 and 0.56 respectively for the FIDAS and TEOM instruments (Figure 2.2b).



**Figure 2.2. Comparison of a) Robust Median NR-PM1 + BC and b) SIRTA NR-PM1 + BC mass concentrations with those of the FIDAS and TEOM PM1 mass concentration.**

For this reason, comparison with the SIRTA instrument seems to be more representative of the NR-PM1 than the robust median of ACSM instruments. Similar to the observations from the z-score calculation, the PUY measured mass concentrations were higher than those from both SIRTA and the FIDAS instrument, with slope values of 1.30 and 1.37 respectively.



**Figure 2.3. Comparison of PUY NR-PM1 + BC with the a) SIRTA NR-PM1 + BC mass concentrations and b) with PM1 mass concentration from FIDAS and TEOM PM1 mass concentration.**

### 3. Optimization of (relative) ionization efficiency values

Following initial intercomparison, instruments were checked, maintained and/or tuned (when needed) during the following week (19<sup>th</sup> to 23<sup>rd</sup> Nov). A series of calibrations were performed on each individual instrument at ACMCC during and after the workshop, using monodisperse (300 nm) ammonium nitrate and ammonium sulfate nebulized particles. The calibration set up is illustrated in Fig. 3.1.

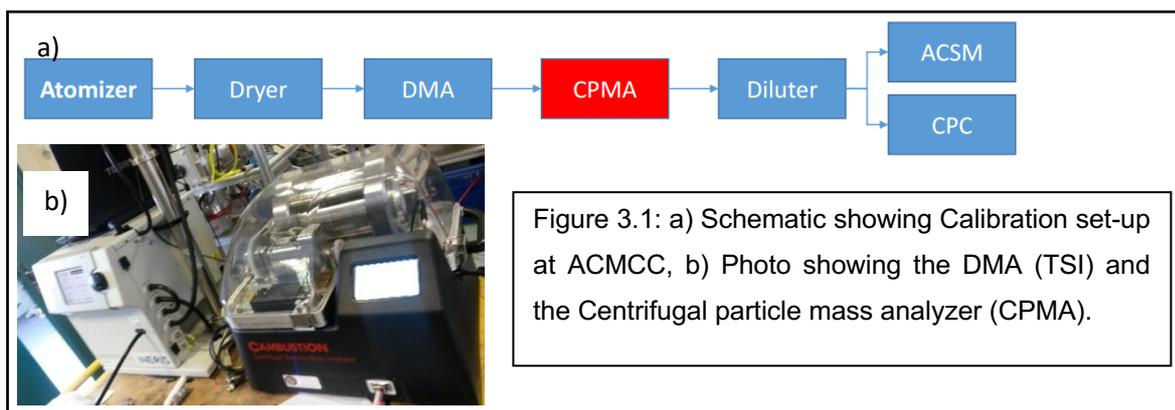


Figure 3.1: a) Schematic showing Calibration set-up at ACMCC, b) Photo showing the DMA (TSI) and the Centrifugal particle mass analyzer (CPMA).

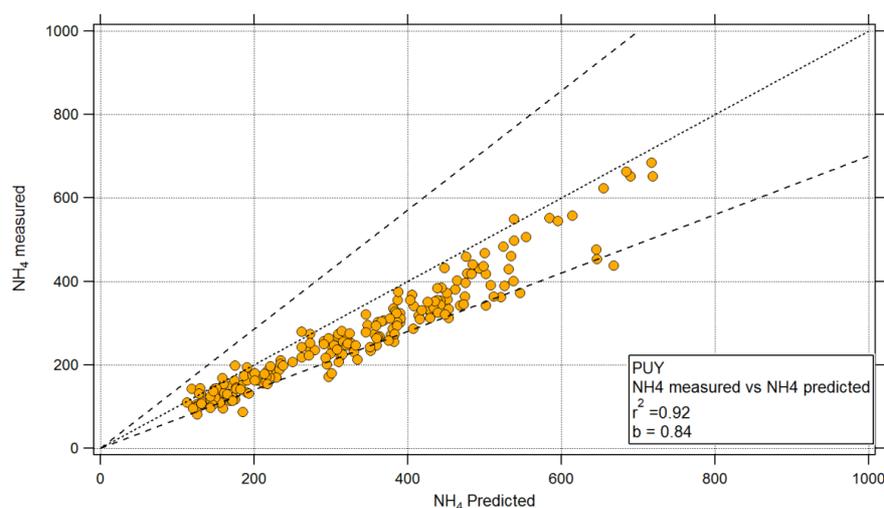
The calibration set up included a differential mobility analyzer (DMA, TSI®) to select particles of diameter 300 nm. This DMA was calibrated prior to use, using 300 nm polystyrene latex spheres (PSL). The aerosol particles were then passed into a Centrifugal particle mass analyzer (CPMA) that separates particles by their actual mass and removes doubly charged aerosol particles. These particles are then passed simultaneously into the ACSM and into a condensation particle counter (CPC). This CPC was calibrated prior to the workshop, based on comparison with an electrometer.

The nitrate response factor (RF) was calculated for each instrument and applied to the raw ACSM signal to obtain quantitative information. This value is determined from a known quantity of a known chemical species that enters into the instrument. The relative ionization efficiency (RIE) is a chemical dependent value that is commonly determined experimentally for the ammonium and sulfate species.

Calibration values provided by PUY for initial intercomparison as well as the ones recommended by the ACMCC for the workshop period (based on results from the full scan calibration mode) are listed in Table 3.1. The  $\text{NH}_4$  measured vs  $\text{NH}_4$  predicted values are illustrated in Figure 3.2, showing good agreement between the two values with a slope of 0.84 with the new RIE  $\text{NH}_4$  value.

| PUY ToF-ACSM13    | RF $\text{NO}_3$ | RIE $\text{NH}_4$ | RIE $\text{SO}_4$ | Ref Airbeam | Ref Temp ( $^\circ\text{C}$ ) |
|-------------------|------------------|-------------------|-------------------|-------------|-------------------------------|
| <b>Initial</b>    | 186              | 3.5               | 0.9               | 445910      | 595                           |
| <b>Calibrated</b> | 200              | 3.12              | 0.8               | 446744      | 596                           |

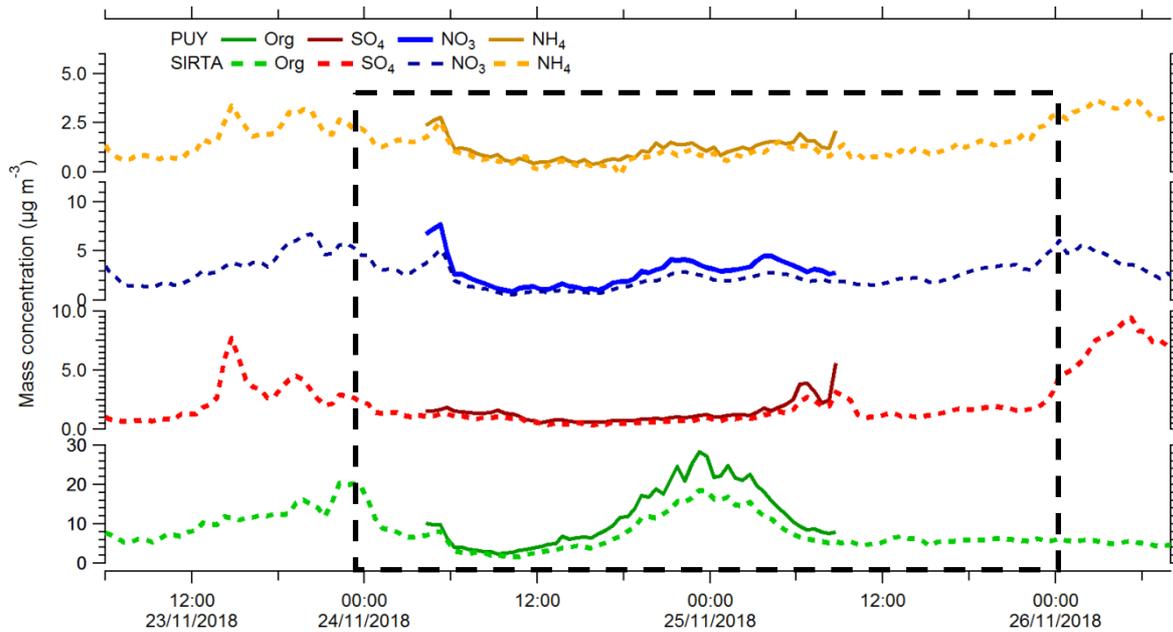
**Table 3.1: Calibration values for the PUY instrument.**



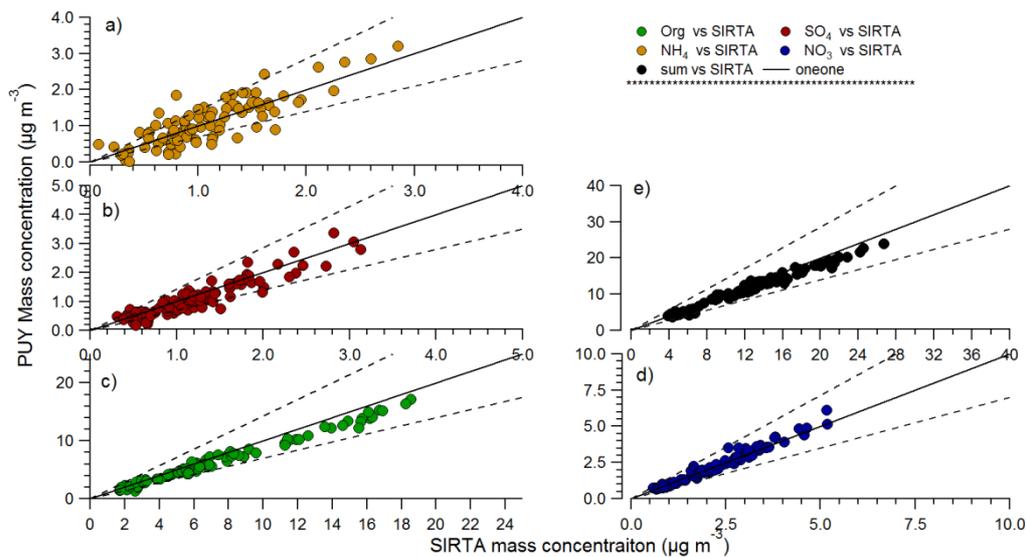
**Figure 3.2  $\text{NH}_4$  measured vs  $\text{NH}_4$  predicted for the PUY instrument using the calibrated RIE  $\text{NH}_4$  values listed in Table 3.2.**

#### 4. Results from the second intercomparison campaign

A second intercomparison campaign took place from the 23<sup>th</sup> to the 26<sup>th</sup> of November, considering calibration results and tuning performed at the ACMCC. The performance of the PUY instrument was again evaluated through comparison with the SIRTA instrument, and later with the robust median of the participating PM1 QACSM instruments. As mentioned earlier, the instrument performance can be considered as acceptable if data points were within  $\pm 30\%$  of these reference values. The PUY instrument shows good temporal agreement with both the median and that of the SIRTA instrument (Fig 4.1), and falls well within  $\pm 30\%$  (Fig 4.2).

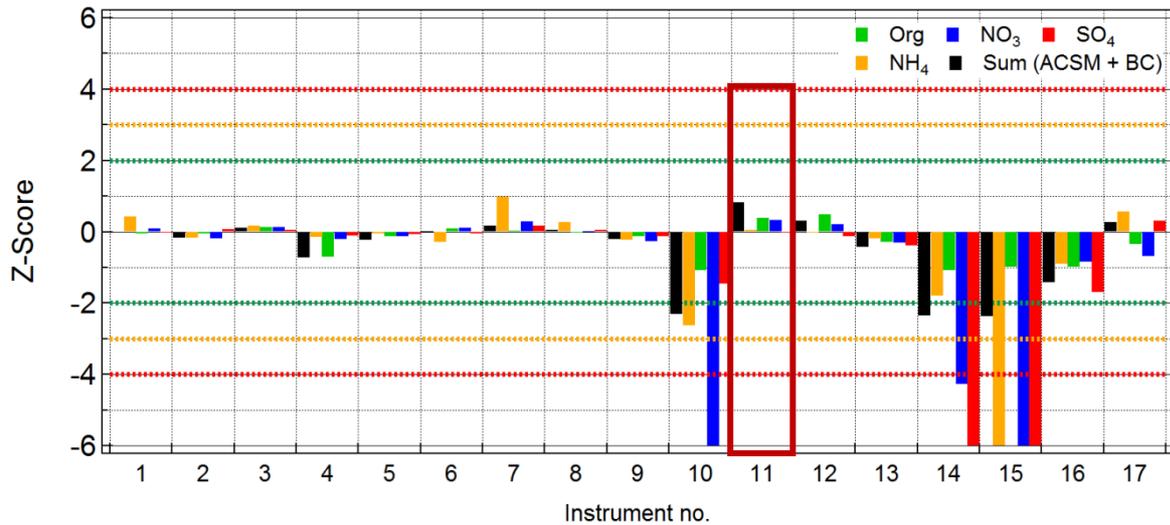


**Figure 4.1. Comparison of PUY with SIRTAs instrument for Ammonia, Nitrate, sulphate, and organic, during the second intercomparison campaign. The highlighted box indicates the intercomparison period (24/11 00hrs to 26/11 00hrs).**



**Figure 4.2. Correlations between different chemical species measured by the PUY and the SIRTAs instrument during the second intercomparison campaign (24<sup>th</sup> Nov 00hrs to 26<sup>th</sup> Nov 00hrs).**

The second method of evaluation was made using the Z-score comparison. As described in section 1, instrument performance is considered acceptable when Z-score values fall between 2 and -2 (indicated by the green lines in Figures 4.3). Figure 4.3 shows the z-score calculated for each instrument using the robust median as a reference. The robust median was calculated as the median of all instruments but outliers and PM<sub>2.5</sub>-inlet ACSMs (i.e., instruments # 10, 14, 15, and 16). The PUY instrument is no. 11 (red rectangle), showing that this instrument is well within acceptable limits of this statistical test.



**Figure 4.3. Z-score calculation for each species measured by the ACSM for each instrument that participated in the second intercomparison campaign (period 24<sup>th</sup> Nov 00hrs to 26<sup>th</sup> Nov 00hrs). The red rectangle highlights the PUY (no.11) instrument.**

## 5. Conclusion

The PUY arrived at the ACMCC in good operational order and compared very well with reference instrument and median values. After calibration and tuning, the instrument performance was improved and was well within the acceptable limits of the Z-score test.

## 6. References

Bahreini, R., Ervens, B., Middlebrook, A. M., Warneke, C., de Gouw, J. A., DeCarlo, P. F., et al. (2009). *J. Geophys. Res.* 114:D00F16, doi:10.1029/2008JD011493.

Crenn, V., Sciare, J., Croteau, P. L., et al., (2015), *Atmos. Meas. Tech.*, 8, 7239-7302, doi:10.5194/amtd-8-7239-2015.

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Middlebrook, A.N., R. Bahreini, J. L. Jimenez, and M. R. Canagaratna (2012) *Aerosol Sci. Tech*, 46:258–271.