Aerosol Chemical Monitor Calibration Center

Intercomparison of Quadrupole Aerosol speciation chemical monitors

Project No.: ACSM-2016-1-6

Basic information

Location of the quality assurance: SIRTA, Lab 705

Delivery date: February 26th, 2016

Setup in the laboratory: February 29th, 2016

Comparison and calibration period: from March 3rd to March 14th, 2016

Principal investigator	Institute	Participant	Instrument
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Contents

1.0 Overview of the intercomparison.

The TROPOS instrument passed the quality standards required as part of the ACTRIS2 network. These requirements include:

1) That the instrument performance is within the acceptable limits evaluated using the Z-score method by ISO 5725-2 compared with the median of all instruments.
2) The instrument performance was within ±30% of the reference instrument.

From March 3rd to March 14th the TROPOS QACSM participated in the ACMCC ACTRIS-2 workshop. The workshop consisted of an entrance intercomparison test and a final intercomparison check. In addition to these ambient measurement intercomparisons, there were a number of different calibrations performed. The calibrations included monodisperse (300 nm) ammonium nitrate and ammonium sulfate solutions, and polydisperse mixtures of ammonium nitrate and ammonium sulfate.

The report is divided into six main sections. The first section shows the status of the reference instruments in the week prior to the measurements period. The second section includes instrumentation on the laboratory setup, and the list of instruments used for the calibration. The third section outlines the error estimation for the ACSM instruments. In the final sections, we show the pre and post intercomparison results as a function of chemical species as well as the calibration results and the optimum settings that were determined for this instrument.

2.0 Reference instrument

The reference instrument was chosen to be the SIRTA instrument. This instrument participated in the previous ACSM intercomparisons and it has not been moved from the site since mid-2013. The instrument is regularly maintained and calibrated by the ACMCC staff. In order to validate this instruments performance it is compared with several other collocated instruments at the site. These instruments include a particle into liquid sampler (PILS (PM1) for inorganic anions (SO_4^{2-}, NO_3^-), and cations (NH_4^+), a sunset OCEC sampler for total OM, and a TEOM–FDMS for total number concentration of submicron particles (PM1) measurements.

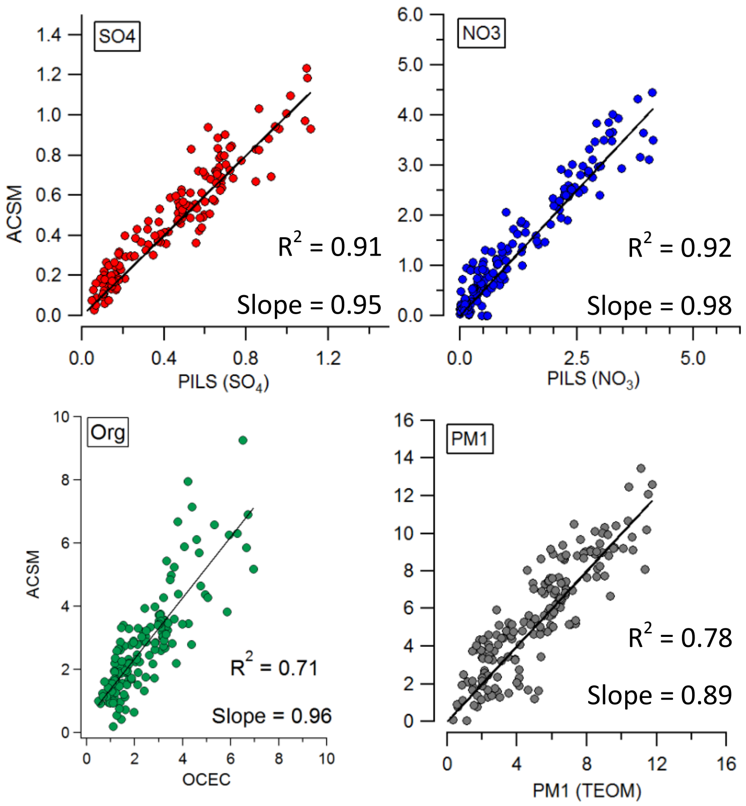

Figure 2.1. Comparison of SO_4 measured by the SIRTA instrument with PILS-SO_4 measurements made at the site, NO_3 measured by the ACSM compared with that measured by the PILS-NO_3, Organic measured by the SIRTA instrument compared with that of the OCEC instrument, and Total PM1 measured by the ACSM compared with that from the TEOM instrument.

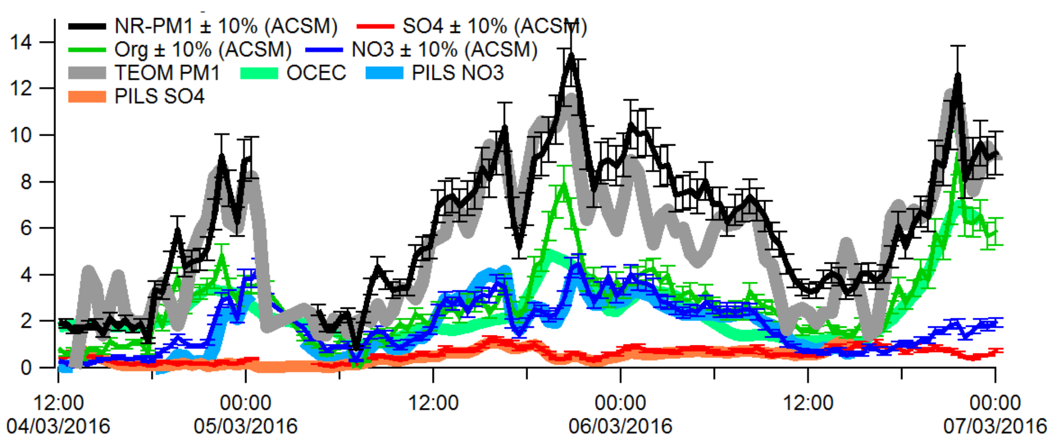

Figure 2.2. Time series comparison of of SIRTA organic, SO_4 and NO_3 species, with co-located online sampling instrumentation.

Over the pre-calibration period we observe that the ACSM instrument agreed very well with the external instrumentation giving slopes ranging between 0.89 and 0.98, and correlations R^2 > 0.78 for all species (Fig. 2.1, 2.2). The supplementary measurements PILS were not chosen as reference instruments since they do not technically measure the same particle types and differences in the measurements could be due to different ambient particle types (refractory vs non-refractory, PM1 vs PM2.5) being measured rather than varying instrument performance.

3.0 Error estimation

An error of 30% was used as the acceptable variation of a test instrument compared with the reference instrument. This error was estimated from a combination of tests performed during the intercomparison campaign. This is a first estimate and further analysis and tests will be performed to provide more accurate error calculations.

The first parameter that was taken into account for the error calculation was the error associated with calibrations (Error 1): reproducibility of the calibration using the same operator and the same calibration set –up. We calculated the calibration repeatability to be 24% between different operators (comparing the previous noted calibration values with those values obtained at the ACMCC), however repeatability of calibrations performed during the ILC exercise by the ACMCC staff and using the same set up were up to 14%. The second identified source of error was the efficiency with which aerosol particles are transmitted through the aerodynamic inlet (Transmission efficiency (TE)) (Error 2). We show in Figure 3.1 the TE for 5 different ACSM instruments measured for diameters from 200 nm up to 600 nm. The maximum variability associated with these measurements was calculated to be 25%. The final source of error that was taken into account is the variability in the chemical dependent collection efficiency (CDCE, Middlebrook et al., (2012) (Error 3). This was calculated independently for each instrument, the variability among these values under the same ambient sampling conditions was 5%.

Combining these errors using Eq 1 gives us a maximum error of 29%, these agrees well with previous estimates of aerodyne AMS instruments (30%) (Middlebrook et al., 2012, Bahreini et al., 2009). Further analysis will be made to improve these estimates.

$$\sqrt{\sum Error1^2 + Error2^2 + Error3^2} \quad \text{(Eq.1)}$$

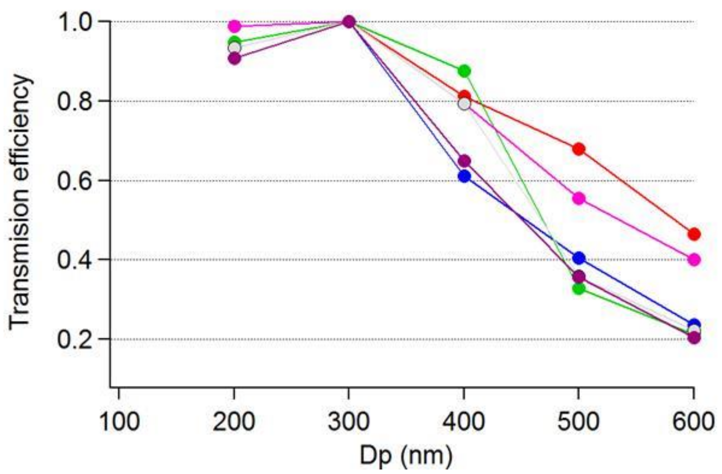

Figure 3.1 Transmission efficiency measured for five different instruments from diameters of 200 nm up to 600 nm.

4.0 Pre-calibration intercomparison

Instruments were installed as shown in Figure 4.1. There were four different tables, each containing three to four instruments. Each table had its own inlet, fitted with a PM 2.5 cyclone. Relative Humidity (RH) was measured at each inlet and never increased above 30%. Most instruments were fitted with an additional nafion dryer. All sampling lines were composed of ½ inch copper tubes and were the same length for each instrument. All instruments sampled 3 l/min from the main inlet line, this flow was controlled by external sample line flow pumps.

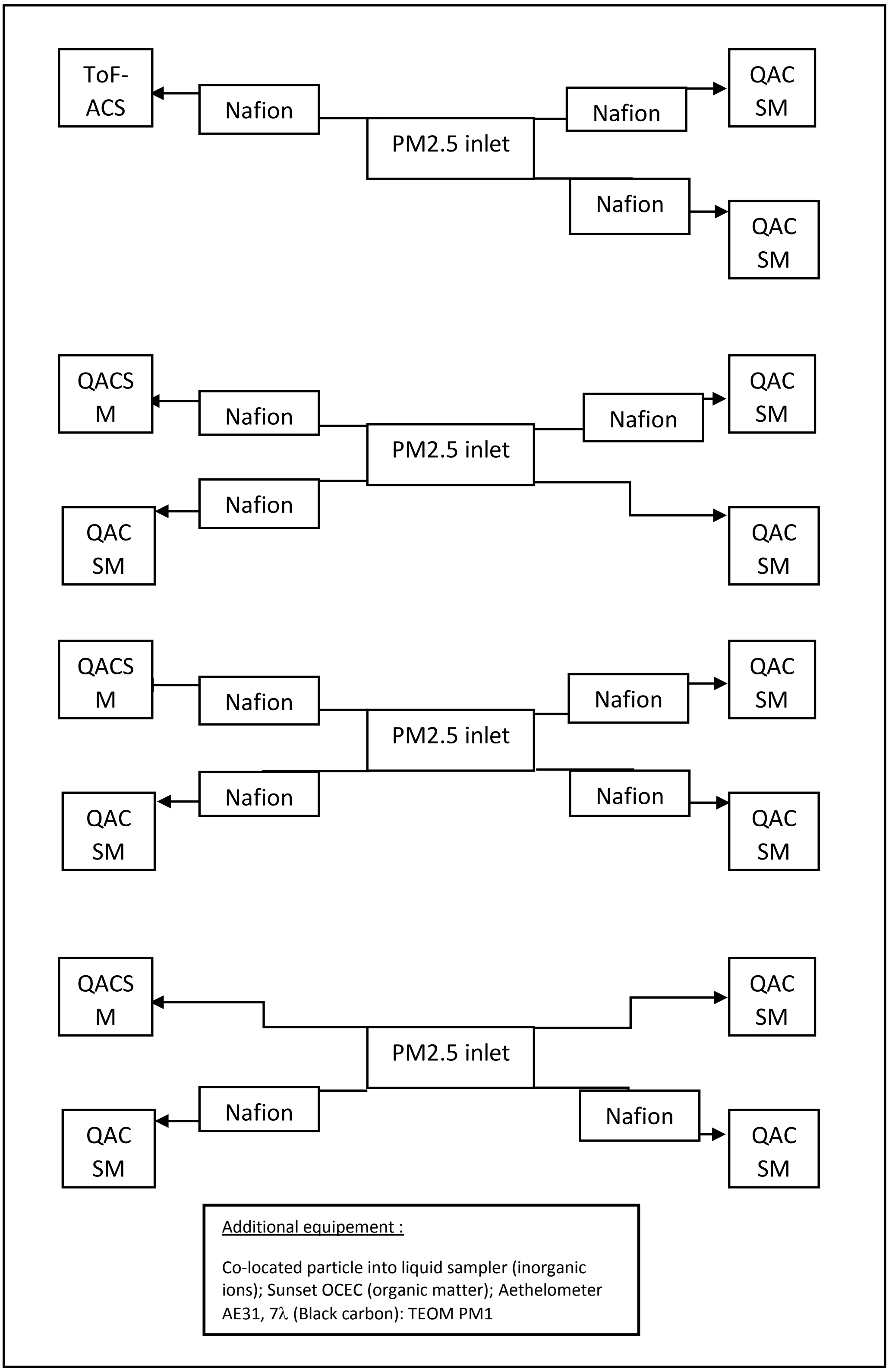

Figure. 4.1 Instrument set up during the intercomparison at the ACMCC.

Instruments were installed at their respective tables and turned on and left sampling at the station from the 4th to the 7th of March 2016. The TROPOS instrument settings and calibration values are listed in table 4.1.

The instrument showed good agreement with the temporal trends of SIRTA reference instrument for total mass concentration nitrate and organic (Fig. 4.2 and 4.3). However, the absolute concentrations of NR-PM1, NH_4, and SO_4 were not in agreement with the reference instrument (Slope: 0.64, 0.37, 0.59, respectively) (Fig 4.3). The NH_4 measured vs predicted show a poor slope suggesting that the relative ionization efficiency (RIE) for the NH_4 is not suitable for this instrument. However, it should be noted that when this instrument was unpacked at the ACMCC the previous acquisition setting did not correctly load. This is likely a reason for the poor 'pre-calibration' comparison. We would advise the PI of this instrument to show NH4 measured vs predicted for this instrument prior to shipment.

Lens pressure	1.367
Detector V	2102
Recent calibration	2016.02.08
NO3 IE	5.2×10^{-11}
NH4 RIE	9.57
SO4	0.54
ACSM DAQ version	2.019
Scan range (amu)	10 – 200
ACSM igor version	6.34

Table 4.1. TROPOS instrument settings prior to calibrations.

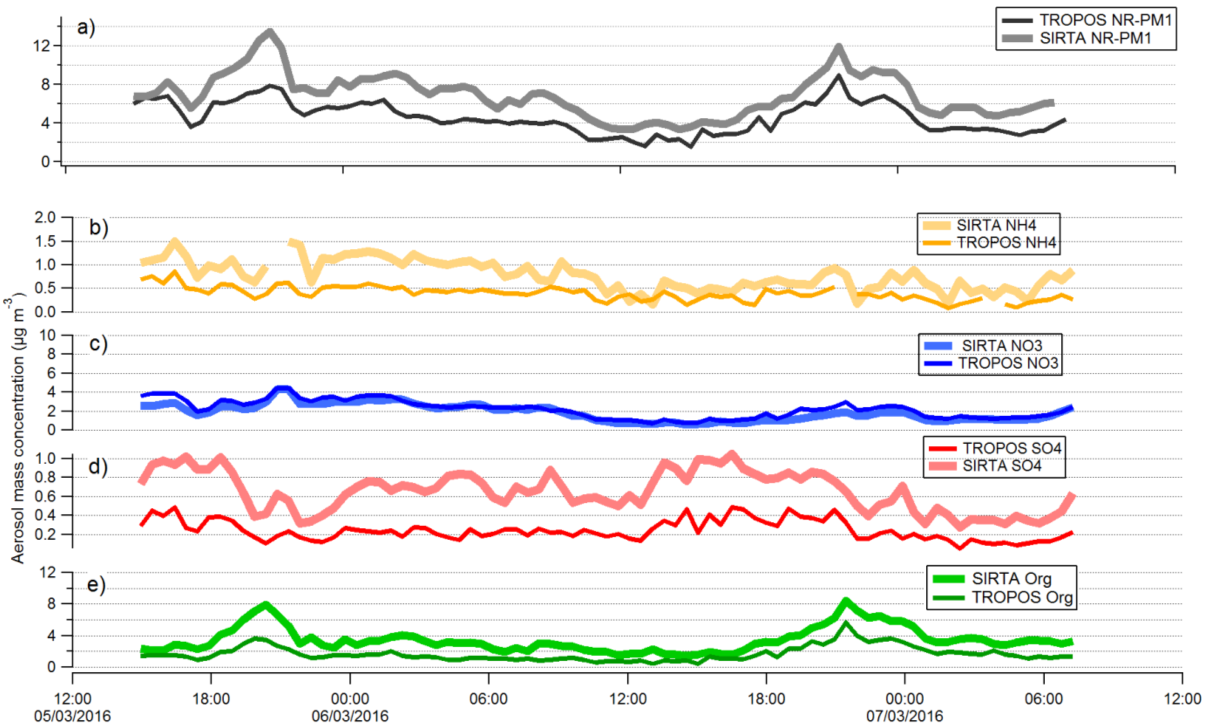

Figure 4.2. a) Comparison of total NR-PM1 mass concentration and of each of the individual species measured by the ACSM, as well as the individual chemical species, b) NH_4, c) NO_3, d) SO_4, and e) Org.

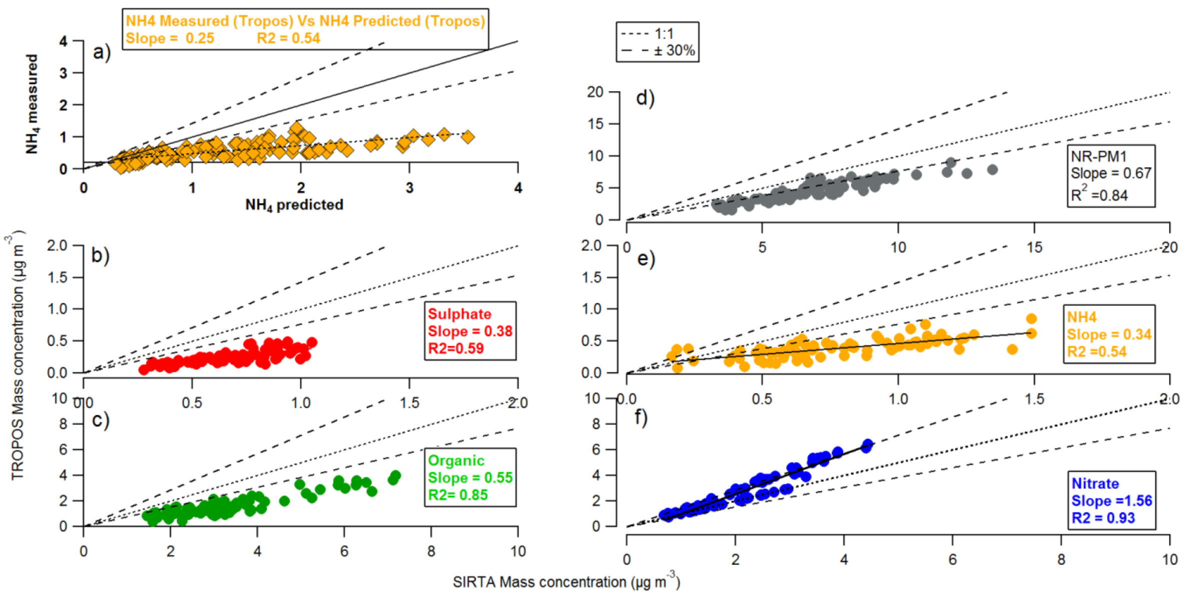

Figure 4.3. a) NH_4 measured vs NH_4 predicted for TROPOS instrument, and comparison of the TROPOS instrument with the SIRTA instrument for b) SO_4, c) Org, d) Total NR-PM1 mass concentration, e) NH_4, and f) NO_3.

5.0 Calibrations

A series of calibrations were performed on each individual instrument. These included: 1) A monodisperse (300 nm) solution of Ammonium nitrate,

2) A monodisperse (300 nm) solution of Ammonium sulfate,

3) Mixtures of Ammonium Sulfate and Ammonium Nitrate (ratios 2:1, 1:2).

The calibration set up for 1) and 2) are illustrated in Fig. 5.

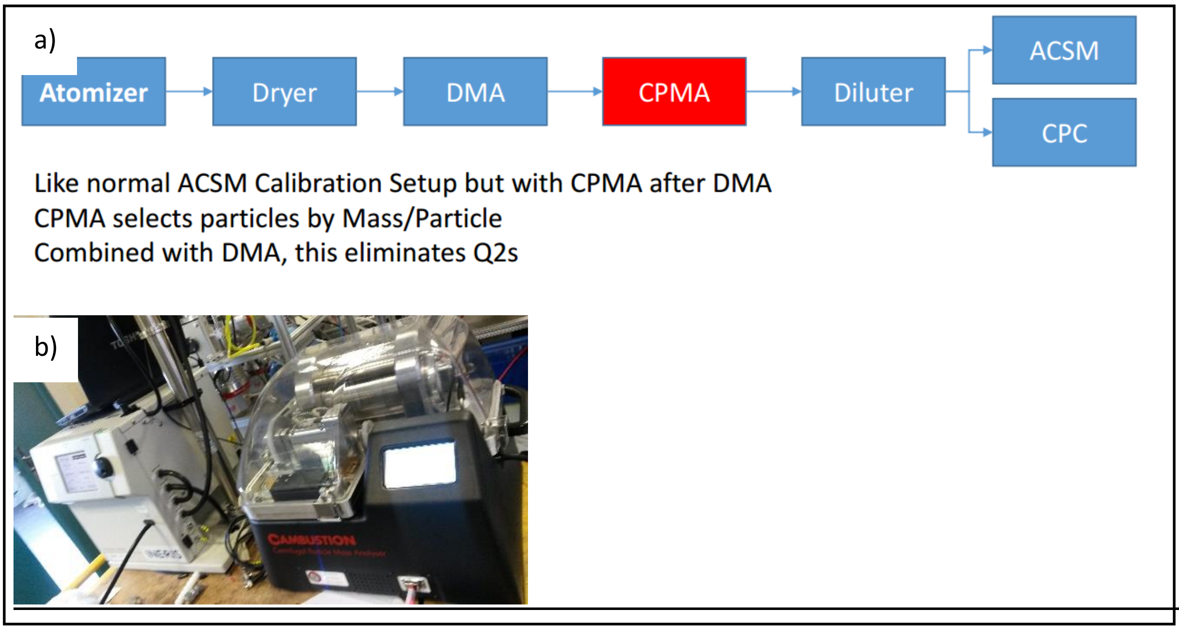

Figure 5.0: a) Schematic showing Calibration set-up, b) Photo showing the DMA (TSI) and the Centrifugal particle mass analyzer (CPMA).

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) (Fig. 5.0).

The response factor (RF) for the ammonium nitrate aerosol particles was calculated using a single salt solution of ammonium nitrate. This was calculated for each instrument and the corresponding ammonium ionization efficiency. The RF is 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 RIE is a chemical dependent value that is applied to different species, and is determined both from the single salt solutions of ammonium nitrate and ammonium sulphate. From these solutions we can calculate a RIE for ammonium and for sulphate.

Serial #	$RFNO_3$	RIENH4 STD	RIESO4 STD	RIESO4 MIX	RIENH4 MIX
TROPOS					
Original	**5.20e-11**	9.57	0.54	**-**	**-**
Calibrated	**6.24e-11**	5.38	0.32	**0.70**	**3.50**

Table 5: Calibration values for the TROPOS instrument for each calibration method. Bold green highlights the recommended values.

The third calibration, which is a relatively new method, uses mixtures of ammonium nitrate and ammonium sulfate. This calibration provides a verification of the RIE ammonium but also the RIE sulfate. This calibration method provides a more robust method to calculate the RIE ammonium since it is determined from two different compounds. Sample solutions are measured using the ambient acquisition mode rather than the previous “calibration mode” so that RIE values are calculated under conditions identical to those when sampling ambient aerosols. It is advised in the future that the mixture calibration is performed at the site. The up to date calibration values are listed in Table 5.

5.1 Post-calibration intercomparison

Once all instruments were calibrated they sampled ambient air for a period of three days, from the 12th to the 14th of March (Fig. 5.1, 5.2). This exercise is necessary to verify that all instruments were working correctly, and that these instruments compared well with the reference instrument and with the median of all instruments after new calibration values were applied.

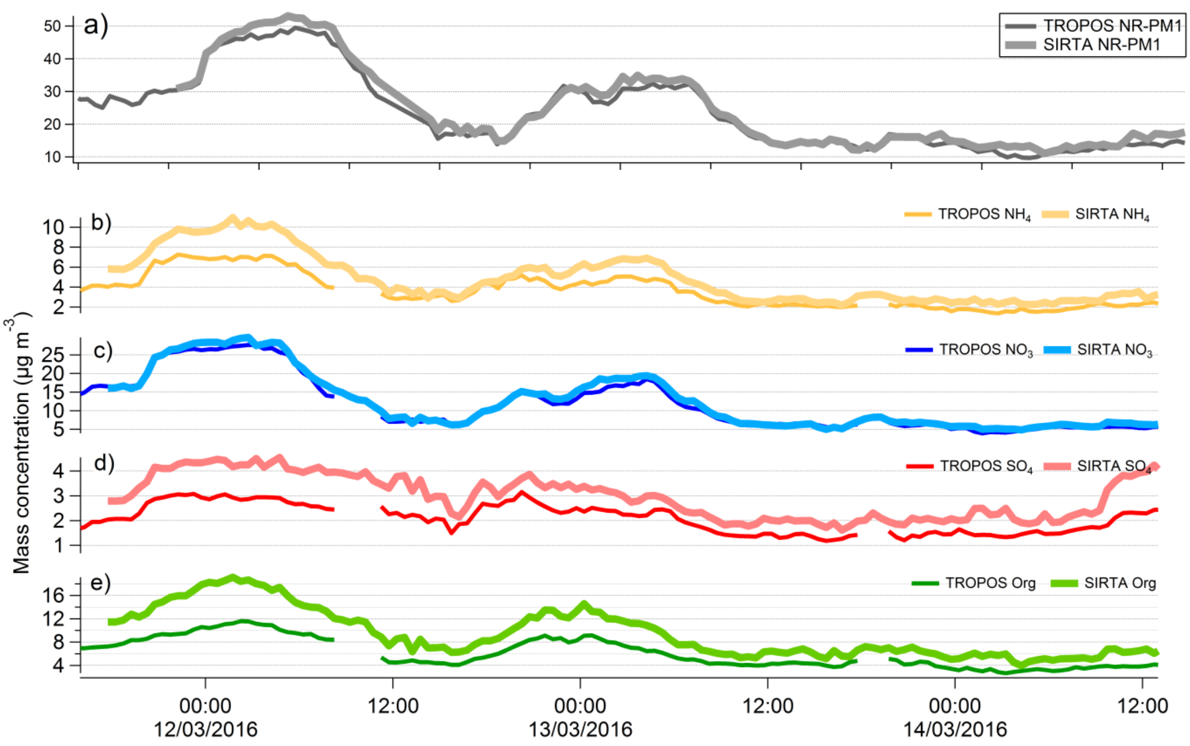

Figure 5.1. Comparison of TROPOS with reference instrument for a) Total PM, b) Ammonia, c) Nitrate, d) Sulphate, and e) Organic.

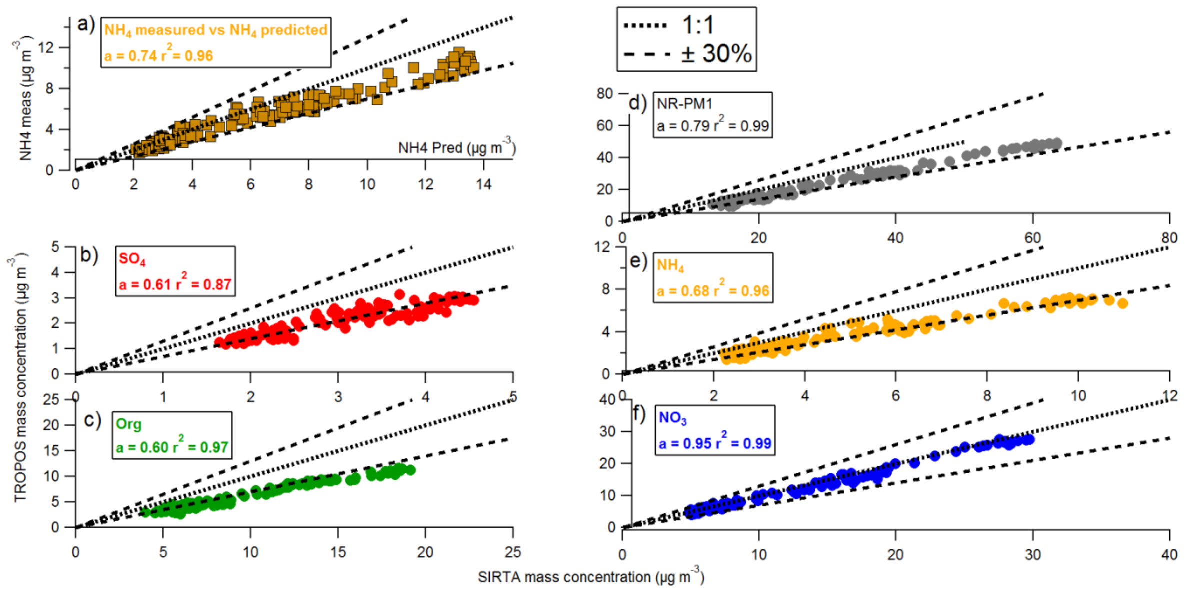

Figure 5.2. a) NH_4 measured vs NH_4 predicted for TROPOS instrument, and comparison of the TROPOS instrument with the SIRTA instrument for b) SO_4, c) Org, d) Total NR-PM1 mass concentration, e) NH_4, and f) NO_3.

The post-calibration intercomparison period showed good temporal agreement between TROPOS instrument and the SIRTA instrument, with total NR-PM1 having a slope of 0.79, and a correlation of R^2 = 0.99 (Fig. 5.2 d)). There was a considerable improvement in the slopes of all species were within the ±30 % boundaries.

5.2 Determining instrument performance

In order to determine whether instruments can be considered to meet the requirements of ACTRIS sampling, we chose to use two independent methods to evaluate each instrument. The first of these methods was to compare each instrument to the reference instrument. The test instrument was deemed to be within acceptable limits if the data points were within ± 30% of the reference instrument values (see section 3.0). The TROPOS instrument, falls close to the limits of these bars and can therefore be considered to have passed the intercomparison (Fig. 5.2). Largest discrepancies were observed with the organic aerosol. Variability in the OA has been documented in previous studies (Crenn et al., 2015, Frohlich et al., 2015, Pieber et al., 2016), and continuing efforts are being invested to better understand the artefacts associated with these signals.

The second method chosen was the Z-score analysis following the standards defined by the international standard organization (ISO). These methods were initially validated in the first ACTRIS1 ACSM intercomparison (Crenn et al., 2015). This method has been evaluated according to ISO 5752-2 and provides a means to evaluate instrument performance relative to a reference instrument and to the median of all instruments participating in the intercomparison. This method has been applied to other European intercomparison exercises (JRC technical intercomparison reports). This approach evaluates if the variations in the different instruments from the reference value fall within a defined criterion. This will allow us to highlight any problems with the Q-ACSM instruments. The Z-score was calculated from the different instruments according to ISO 5752-2 (2005) (Eq.2).

$$Z_i = \frac{X_I - X^*}{\sigma_*}$$

Eq. 2

According to this test, instrument performance is considered acceptable when values fall between 2 and -2 (indicated by the green lines in Figures 5.3). Values falling between 2 and 3, may need to be examined. Figure 5.3 shows the z-score calculated for each instrument using the median of all instruments as a reference. The TROPOS instrument is no. 11 (red rectangle), showing that this instrument is within acceptable limits of this statistical test.

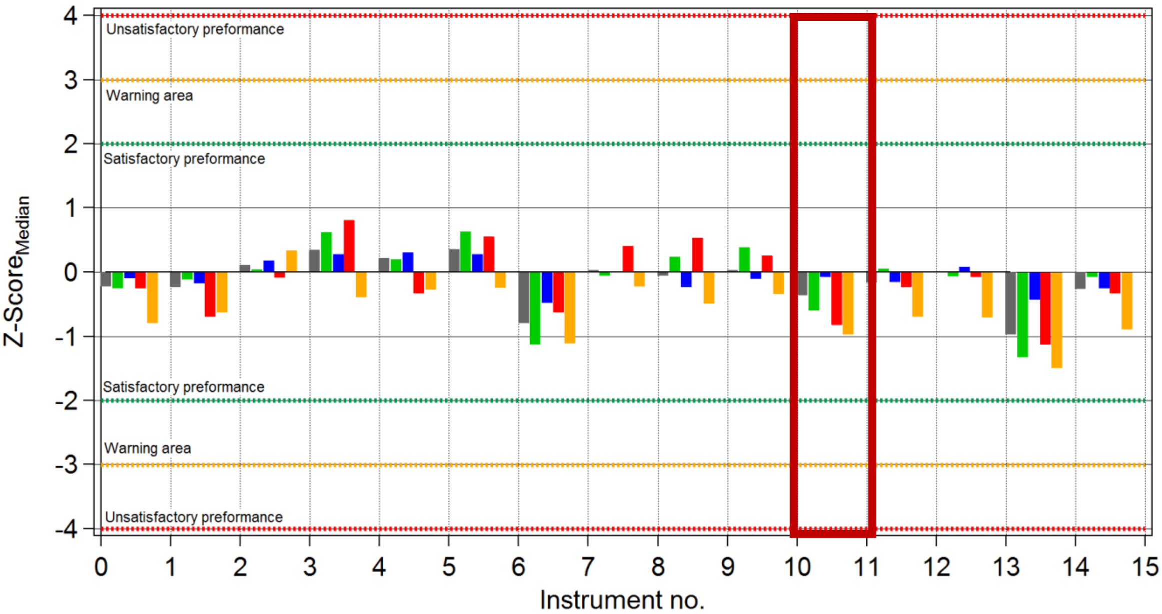

Figure 5.3: Z-score calculation for each species measured by the ACSM for each instrument that participated in the intercomparison. These values are compared with the median value of all instruments. The red rectangle highlights the TROPOS instrument.

6.0 Conclusion

Results from the post-calibration intercomparison indicate that this instrument is within the acceptable limits (±30% of the reference instrument) and using the z-score evaluation method (ISO 5752), this instrument is considered to have satisfactory performance. The pre-calibration exercise was not successful for this instrument due to problems during the installation at the ACMCC. The PI of this instrument should provide plots of NH_4 measured vs NH_4 predicted to show that the instrument was performing in a satisfactory way prior to calibration.

New corrections and up to date fragmentation tables will be developed in collaboration between the ACMCC and Aerodyne and made available in the coming months. These will be shared amongst the ACTRIS community.

7.0 References

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