



# Supplement of

# ACTRIS ACSM intercomparison – Part I: Reproducibility of concentration and fragment results from 13 individual Quadrupole Aerosol Chemical Speciation Monitors (Q-ACSM) and consistency with Time-of-Flight ACSM (ToF-ACSM), High Resolution ToF Aerosol Mass Spectrometer (HR-ToF-AMS) and other co-located instruments

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# 1 Appendix A. Ambient air measurements

- 2 Table A1.
- 3 Average values  $(\pm 1\sigma)$  of ACSM diagnostic parameters (Airbeam, chamber temperature, inlet
- 4 pressure and vaporizer temperature).

ACSM #	<b>Airbeam</b> (10 <sup>-7</sup> )	Chamber temperature (°C)	Inlet Pressure (Torr)	Vaporizer temperature (°C)	
#1	$1.35\pm0.020$	$37 \pm 1.5$	$1.33\pm0.02$	$601.0\pm8.3$	
#2	$0.95\pm0.033$	$33\pm0.4$	$1.33\pm0.01$	$603.5\pm0.49$	
#3	$0.95\pm0.049$	$40 \pm 3.1$	$1.25\pm0.02$	$595.3\pm3.1$	
#4	$0.90\pm0.054$	$33\pm0.5$	$1.23\pm0.01$	$601.7\pm0.40$	
#5	$0.97\pm0.025$	$35\pm0.7$	$1.49\pm0.01$	$586.5\pm3.1$	
#6	$0.80 \pm 0.115$	$33 \pm 0.4$	$1.20\pm0.01$	$607.9\pm7.8$	
#7	$1.03\pm0.043$	$36 \pm 1.1$	$1.40\pm0.01$	$600.9\pm2.42$	
#8	$0.89 \pm 0.068$	$31 \pm 0.5$	$1.33\pm0.01$	$594.0\pm3.4$	
#9	$0.94\pm0.032$	$37\pm0.7$	$1.21\pm0.10$	$596.6\pm0.24$	
#10	$1.04\pm0.024$	$35 \pm 0.4$	$1.22\pm0.01$	$596.6\pm0.27$	
#11	$0.96\pm0.085$	$36\pm0.6$	$1.23\pm0.01$	$599.8\pm0.21$	
#12	$0.92\pm0.042$	$30 \pm 0.6$	$1.31\pm0.01$	$603.4\pm0.22$	
#13	$0.93 \pm 0.168$	$31 \pm 0.4$	$1.32 \pm 0.01$	590.8 ± 1.6	



2 Figure A1. Temporal coverage of co-located instruments deployed during the intercomparison

3 study.

## 1 Appendix B. Effects of the use of individual ACSM sulfate relative ion

## 2 efficiencies

#### 3 Use of sulfate relative ion efficiency values obtained from the first calibration phase

4 It is recalled here that  $RF_{NO3}$ ,  $RIE_{NH4}$  and  $RIE_{SO4}$  values obtained from calibrations performed 5 at the beginning of the study were discarded, and that only RF<sub>NO3</sub> and RIE<sub>NH4</sub> could be estimated from calibrations performed at the end of campaign. A default RIE<sub>SO4</sub> value of 1.2 6 (RIE<sub>SO4.def</sub>) was then applied to calculate sulfate mass concentrations. The reasons of this 7 choice are given in Sect. 3.1.2. Here, we present the effect of ACSM-independent RIE<sub>SO4</sub> 8 9 (RIE<sub>SO4</sub> values measured at the beginning of the intercomparison exercise for each ACSM, noted  $RIE_{SO4}^{*}$  thereafter) to calculate the SO<sub>4</sub> mass concentrations. The  $RIE_{SO4}^{*}$ ,  $RIE_{SO4,def}$ 10 values and RIE<sub>SO4.def</sub>-to-RIE<sub>SO4</sub><sup>\*</sup> ratios are given in Table B1, respectively. RIE<sub>SO4.def</sub>-to-11  $RIE_{SO4}$  ratios varied by a factor of 2 ranging from 1.24 (ACSM #5) to 2.50 (ACSM #2). 12 The temporal variability of the median mass concentrations and range (minimum, maximum) 13 of SO<sub>4</sub> measured by the 13 Q-ACSMs and linear correlation plots for SO<sub>4</sub> mass 14 concentrations obtained with  $RIE_{SO4}^*$  values are shown in Fig. B1, and Fig. B2, respectively. 15 Slopes varied from 0.58 (ACSM #7) to 1.88 (ACSM #2) while they only varied from 0.62 16

17 (ACSM #10) to 1.47 (ACSM #5) with a constant value of 1.2, highlighting a higher

18 dispersion of SO<sub>4</sub> measurements using individual ACSM RIE<sub>SO4</sub> values.

# 1 Table B1.

ACSM #	RIE <sub>NH4,meas</sub>	RIE <sub>SO4,def</sub>	RIE <sub>SO4</sub> *	$\operatorname{RIE}_{\mathrm{SO4,def}}/\operatorname{RIE}_{\mathrm{SO4}}^*$
#1	3.37	1.2	0.82	1.46
#2	14.72	1.2	0.48	2.50
#3	5.48	1.2	0.71	1.69
#4	8.98	1.2	0.70	1.71
#5	3.42	1.2	0.97	1.24
#6	4.72	1.2	0.70	1.71
#7	7.24	1.2	0.87	1.38
#8	6.45	1.2	0.62	1.94
#9	3.56	1.2	0.76	1.58
#10	7.79	1.2	0.56	2.14
#11	3.17	1.2	0.67	1.79
#12	3.83	1.2	0.71	1.69
#13	9.36	1.2	0.87	1.38

2 Average  $RIE_{NH4}$  and  $RIE_{SO4}$  values determined from ACSM calibrations



Figure B1. Averaged sulfate mass concentrations measured by the 13 Q-ACSMs using an instrument-dependent  $\text{RIE}_{SO4}^*$ . Dark red line and color area correspond to the median of ACSMs and the min-max range, respectively.



Figure B2. Scatter plots of sulfate mass concentrations in  $\mu g \text{ m}^{-3}$  measured by each ACSM versus the median of all the 13 Q-ACSMs, for which an instrument-dependent  $\text{RIE}_{SO4}^*$  was applied. Dotted line is the 1:1 line. Full lines represent the orthogonal distance regression fits

5 with zero intercept.

## 1 Use of sulfate relative ionization efficiency values calculated assuming full neutralization

# 2 of secondary inorganic aerosols

For each instrument, the  $RIE_{SO4}$  value needed to obtain full neutralization of secondary inorganic aerosols ( $RIE_{SO4,neut}$ ) could be estimated by fitting ACSM measured and predicted SO<sub>4</sub> values (SO<sub>4,meas</sub> and SO<sub>4,pred</sub>, respectively), where SO<sub>4,pred</sub> is the estimated value of SO<sub>4</sub> and calculated as follows:

$$SO_{4,pred} = \frac{NH_{4,meas} - \left(\frac{MW(NH_4)}{MW(NO_3)}\right)NO_{3,meas} - \left(\frac{MW(NH_4)}{MW(Cl)}\right)Cl_{meas}}{2\left(\frac{MW(NH_4)}{MW(SO_4)}\right)}$$
(B1)

where MW(s) is the Molecular Weight of the chemical species (s), SO<sub>4,meas</sub>, NO<sub>3,meas</sub>, Cl<sub>meas</sub>,
and NH<sub>4,meas</sub> are the SO<sub>4</sub>, NO<sub>3</sub>, Cl, and NH<sub>4</sub> mass concentrations measured by the ACSMs,
respectively.

 $RIE_{SO4,neut}$  is then estimated dividing the RIE default value ( $RIE_{SO4,def} = 1.2$ ) by the slope of 10 11 SO<sub>4,pred</sub> vs. SO<sub>4,meas</sub>. RIE<sub>NH4,meas</sub>, RIE<sub>SO4,def</sub>, RIE<sub>SO4,neut</sub> and RIE<sub>SO4,def</sub>-to-RIE<sub>SO4,neut</sub> values 12 used/calculated for each ACSM are given in Table B2. RIE<sub>SO4.def</sub>-to-RIE<sub>SO4.neut</sub> ratios varied significantly from 0.13 (ACSM #2) to 4.81 (ACSM #9). Although RIE<sub>SO4</sub> measured values 13 14 above the default value of 1.2 have been recently reported in the literature for a few 15 calibrations conducted by participants (Petit et al., 2015; Ripoll et al., 2015) those values were quite close to the default 1.2 value (i.e., 1.25 and 1.26, respectively). By contrast, very 16 17 low/high RIE<sub>SO4.neut</sub> obtained here for some instruments does not make sense and can only be discarded. 18

19 The temporal variability of the median mass concentrations and range (minimum, maximum) 20 of SO<sub>4</sub> measured by the 13 Q-ACSMs and linear correlation plots for SO<sub>4</sub> mass concentrations obtained with RIE<sub>SO4.neut</sub> values are shown in Fig. B3, and Fig. B4, 21 22 respectively. Slopes varied from 0.13 (ACSM #4) to 2.44 (ACSM #9) while they only varied 23 from 0.62 (ACSM #10) to 1.47 (ACSM #5) with a constant value of 1.2, again highlighting a 24 higher dispersion of SO<sub>4</sub> measurements using individual ACSM RIE<sub>SO4</sub> values. It should be 25 noted that the methodology described in the present subsection to estimate  $RIE_{SO4}$  (a 26 posteriori and using ambient data) could be attempted here due to previous data showing full 27 neutralization of both sulfate and nitrate by ammonium in the Paris area and during this 28 period of the year (e.g. Bressi et al., 2013). Nevertheless, we do not mean that the use of such 29 a methodology should be promoted for  $RIE_{SO4}$  calculation within future studies.

# 1 Table B2.

ACSM #	RIE <sub>NH4,meas</sub>	RIE <sub>SO4,def</sub>	RIE <sub>SO4,neut</sub>	RIE <sub>SO4,def</sub> / RIE <sub>SO4, neut</sub>
#1	3.37	1.2	0.61	1.96
#2	14.72	1.2	9.40	0.13
#3	5.48	1.2	0.84	1.43
#4	8.98	1.2	8.30	0.14
#5	3.42	1.2	0.59	2.04
#6	4.72	1.2	0.54	2.22
#7	7.24	1.2	2.32	0.52
#8	6.45	1.2	0.47	2.54
#9	3.56	1.2	0.25	4.81
#10	7.79	1.2	3.36	0.36
#11	3.17	1.2	0.36	3.37
#12	3.83	1.2	0.48	2.48
#13	9.36	1.2	5.43	0.22

2 Average RIE values calculated assuming ion full neutralization of ambient aerosols



2 Figure B3. Averaged sulfate mass concentrations predicted for the 13 Q-ACSMs using an

3 instrument-dependent  $RIE_{SO4,neut}$ . Dark red line and color area correspond to the median of

4 ACSMs and the min-max range, respectively.



Figure B4. Scatter plots of sulfate mass concentrations in  $\mu g \ m^{-3}$  predicted for each ACSM 2 3 versus the median of all the 13 Q-ACSMs, for which an instrument-dependent RIE<sub>SO4,neut</sub> was 4 applied. The median of all the 13 Q-ACSMs was calculated as the median value of the 5 SO<sub>4,pred</sub> concentrations of each ACSM. Many data points were discarded here, due to high 6 uncertainties associated with low NH<sub>4</sub> mass concentrations that may led to negative SO<sub>4,pred</sub> 7 values calculated from Eq. (B1). Some negative SO<sub>4,pred</sub> were also obtained for periods with 8 high concentrations of NH<sub>4</sub>NO<sub>3</sub> and resulted from high uncertainties associated by the 9 difference of two elevated and close concentrations (e.g. [NH<sub>4</sub>] - [NH<sub>4</sub>] from NH<sub>4</sub>NO<sub>3</sub>). This is particularly true for ACSM #2 and 13, and to a lesser extent for ACSM #4, 7 and 10. 10 11 Dotted line is the 1:1 line. Full lines represent the orthogonal distance regression fits with zero 12 intercept.

## **1** Appendix C. ACSM data correction

## 2 <u>Collection efficiency (CE)</u>

The calculation of mass concentrations is depending on a collection efficiency (CE) for both ACSMs and HR-ToF-AMS measurements. The CE correction is accounting for (i) particle bouncing at the inverted-conical vaporizer inducing an incomplete detection of aerosol species (Matthew et al., 2008) (ii) particle losses in the aerodynamic lenses (iii) broadening of the particle beam (Huffman et al., 2005), and (iv) several factors such as high aerosol acidity, ammonium nitrate mass fraction (ANMF) and organic liquid contents and/or relative humidity (Middlebrook et al., 2012). The ANMF is calculated as follows:

ANMF = 
$$\frac{(80/62)NO_3}{(NH_4 + SO_4 + NO_3 + Cl + OM)}$$
(C1)

10 where NH<sub>4</sub>, SO<sub>4</sub>, NO<sub>3</sub>, Cl, and OM are the measured aerosol ammonium, sulfate, nitrate,

11 chloride, and organic mass concentrations (in  $\mu g m^{-3}$ ).

12 In the present study, a composition-dependent CE (CE<sub>ANMF</sub>) was calculated from the

13 following Eqs. (C2) and (C3), adapted from Middlebrook et al. (2012) parameterizations:

$$CE_{ANMF} = 0.0833 + 0.9167 \times ANMF$$
 (C2)

$$CE = \max(0.5, CE_{ANMF})$$
(C3)

14 The temporal variability of the CE we have used during our study is presented in the Fig. C1,15 below.



2 Figure C1. Time series of ACSM collection efficiency (CE) applied to the 13 Q-ACSMs

adapting the procedure given in Middlebrook et al. (2012). The median and the min-max
range of the 13 Q-ACSMs are presented in dark black lines and light grey area, respectively.

# **1** Appendix D. Z-score analysis parameters

# 2 Table D1.

- 3 Statistical analysis values used within Z-score calculations for NR-PM<sub>1</sub> mass concentrations and their major components (OM, NO<sub>3</sub>, SO<sub>4</sub>,
- 4 NH<sub>4</sub>, and Cl), expressed in  $\mu$ g m<sup>-3</sup>, obtained from the data of the 13 Q-ACSMs (N = 780). Raw data values are given for information, while
- 5 robust approach values are those actually used in the present study.

	Raw data <sup>a</sup>				Robust approach <sup>b</sup>				
	Mean value	Standard deviation ( $\sigma$ )	Variation coefficient (%)	Robust mean (x*)	Robust standard deviation (s*)	Recalculated standard deviation $(\sigma_p)^{c}$	Standard deviation of the assigned value (µ*)	Relative confidence interval (%)	
NR-PM <sub>1</sub>	15.7	2.58	16.5	16.9	1.56	1.68	0.616	20.9	
ОМ	6.57	1.19	18.1	6.55	1.22	1.29	0.423	40.6	
NO <sub>3</sub>	5.29	0.892	16.9	5.20	0.770	0.823	0.290	33.0	
$SO_4$	1.28	0.334	26.0	1.27	0.358	0.378	0.124	61.2	
$\mathrm{NH}_4$	2.38	0.973	40.9	2.28	0.817	0.873	0.308	79.6	
Cl	0.136	0.160	117	0.186	0.102	0.109	0.039	122	

6 <sup>a</sup> formula of raw data parameters are given in ISO 5725-2

7 <sup>b</sup> formula of robust approach parameters are available in ISO 5725-5 and ISO 13528

8 <sup>c</sup> calculated from the quadratic sum of s\* and  $\mu$ \* because the number of ACSMs is below 16

- 9 Appendix E. ACSM standard diagnostic ion plots for each ACSM and additional
- 10 statistical Z-score results



Figure E1. Standard diagnostic ion plots of ACSM  $NH_4$  m17 vs. m16. Orthogonal linear regression fits were plotted with zero intercept.



13 Figure E2. Standard diagnostic ion plots of ACSM NO<sub>3</sub> m46 vs. m30. Orthogonal linear

14 regression fits were plotted with zero intercept.



15 Figure E3. Standard diagnostic ion plots of ACSM SO<sub>4</sub> m64 vs. m48. Orthogonal linear

16 regression fits were plotted with zero intercept.



Figure E4. Standard diagnostic ion plots of ACSM Org m44 vs. m43. Orthogonal linearregression fits were plotted with zero intercept.



Figure E5. Relative deviations to the median (RDM) of ACSM concentrations and standard
diagnostic ion slopes for (a) OM (m44 vs. m43), (b) NH<sub>4</sub> (m17 vs. m16), (c) NO<sub>3</sub> (m46 vs.
m30), and (d) SO<sub>4</sub> (m64 vs. m48, m80 vs. m48, m81 vs. m48 and m98 vs. m48) obtained
from orthogonal distance regression fits with zero intercept.







Figure E6. Statistical Z-score results for major ACSM fragments associated to (a) inorganics (m/z 16 and 17 for ammonium, m/z 30 and 46 for nitrate, and m/z 48, 64, 80, 81, and 98 for sulfate) and (b) organic matter (m/z 29, 43, 44, 55, 57, 60, and 73).



2 Influence of a time-dependent density on SMPS PM<sub>1</sub> mass concentrations and comparability with ACSM PM<sub>1</sub>.

Figure F1. (a) Time series of the time-dependent density (red circle dots) and  $PM_1$  mass concentrations in  $\mu g m^{-3}$  measured by the HR-ToF-AMS (dotted grey line) and the median of the 13 Q-ACSMs (solid black line) and (b) scatter plots of  $PM_1$  mass concentrations measured by the median of the 13 Q-ACSMs vs. SMPS  $PM_1$  mass concentrations calculated using a time-dependent density.

#### Scatter plots between ACSM and co-located online instruments



 $a^{a}$ : PM<sub>1</sub> mass was determined from the sum of all non-refractory components (OM, NO<sub>3</sub>, SO<sub>4</sub>, NH<sub>4</sub>, and Cl) and EBC mass concentrations. Moreover, ACSM, ToF-AMS, and HR-ToF-AMS mass concentrations were corrected assuming a time-dependent CE according to the procedure described by Middlebrook et al. (2012); <sup>b</sup>: A mass scattering efficiency of 2.5 m<sup>2</sup> g<sup>-1</sup> was used to reconstruct PM<sub>1</sub> mass (Titos et al., 2012); <sup>c</sup>: PM<sub>1</sub> mass was calculated using an averaged aerosol density of 1.6 based on the NR-PM<sub>1</sub> mass composition measured by HR-ToF-AMS.

6 Figure F2. PM<sub>1</sub> correlation plots between instruments deployed during the intercomparison study. All the concentrations in  $\mu$ g m<sup>-3</sup> were 3-h averaged 7 (*N* = 780). Black solid and dotted lines represent the orthogonal distance regression with non-zero intercept fits and 1:1 lines, respectively.

#### 1 Optical mass closure

The reconstruction of the light scattering coefficient was performed following the same methodology as given in Sciare et al. (2008). Briefly, a simple model assuming an external mixing of the particles with constant dry mass scattering efficiencies and constant aerosol types can be used here to reconstruct the light scattering coefficient ( $\sigma_{sp}$ ), as follows:

$$\begin{aligned}
6 \quad \sigma_{sp} &= \alpha_{ions} f(RH)([(NH_4)_2 SO_4] + [NH_4 NO_3]) + \alpha_{POM} [POM] + \alpha_{sea \ salt} [sea \ salt] + \\
7 \quad \alpha_{dust} [dust]
\end{aligned}$$
(F1)

where  $\alpha_s$  represents the mass scattering efficiency of the chemical species (s). It is assumed 8 here that  $(NH_4)_2SO_4$  and  $NH_4NO_3$  have a mass scattering efficiency of 3 m<sup>2</sup> g<sup>-1</sup> while 9 particulate organic matter and sea salt have mass scattering of 3.9 and 4.3  $m^2 g^{-1}$ , respectively. 10 The light scattering contribution of dust was neglected here due to both their low 11 12 concentrations and mass scattering efficiencies. A constant enhancement factor, f(RH), was 13 taken as equal to 1 after checking that the nephelometer measurements ( $\lambda = 525$  nm) were not 14 significantly affected by water uptake onto aerosols. The RH was kept below 40% during the 15 whole study. The light scattering measured by the latter instrument was then compared to the reconstructed light scattering (Fig. F3). A good agreement was observed ( $r^2 = 0.83$ ; 16 17 slope = 0.93). The difference may be due to propagation uncertainties associated with the 18 measurements of the different species by the different techniques (i.e., nephelometer, OCEC 19 Sunset analyser, ACSM) and the estimation of the mass scattering coefficients biases the 20 reconstructed light scattering values.



22 Figure F3. Optical mass closure calculated between the reconstructed versus measured  $\sigma_{sp}$ .

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