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# Performance of a corona ion source for measurement of sulfuric acid by chemical ionization mass spectrometry

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## Abstract

The performance of an ion source based on corona discharge has been studied. This source is used for the detection of gaseous sulfuric acid by chemical ionization mass spectrometry (CIMS) through the reaction of  $\text{NO}_3^-$  ions with  $\text{H}_2\text{SO}_4$ . The ion source is operated under atmospheric pressure and its design is similar to the one of a radioactive (Americium 241) ion source which has been used previously. Our results show that the detection limit for the corona ion source is sufficiently good for most applications. For an integration time of one minute it is  $\sim 6 \times 10^4$  molecules of  $\text{H}_2\text{SO}_4$  per  $\text{cm}^3$ . In addition, only a small cross-sensitivity to  $\text{SO}_2$  has been observed for concentrations as high as 1 ppmv in the sample gas. This low sensitivity to  $\text{SO}_2$  is achieved even without the addition of an OH scavenger. When comparing the new corona ion source with the americium ion source for the same provided  $\text{H}_2\text{SO}_4$  concentration, both ion sources yield almost identical values. These features make the corona ion source investigated here favorable over the more commonly used radioactive ion sources for most applications where  $\text{H}_2\text{SO}_4$  is measured by CIMS.

## 1 Introduction

The measurement of gaseous sulfuric acid is important since  $\text{H}_2\text{SO}_4$  is one of the key compounds responsible for atmospheric new particle formation (Curtius, 2006; Kulmala and Kerminen, 2008). The nucleation of particles has been observed in many places around the world on ground-based measurement sites as well as in the free troposphere (Kulmala et al., 2004). In most cases the formation rate of new particles correlates with the concentration of sulfuric acid (Yu and Turco, 2001; Fiedler et al., 2005; Kuang et al., 2008). The concentration of  $\text{H}_2\text{SO}_4$  during atmospheric nucleation events is usually between  $10^6$  and  $10^7$  molecules per  $\text{cm}^3$  (Sipilä et al., 2010), i.e. in the sub-ppt range under standard conditions. Therefore, the precise and accurate measurement of sulfuric acid is essential for studying new particle formation under atmospheric conditions as well as during chamber experiments.

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For the real-time measurement of sulfuric acid, chemical ionization mass spectrometry (CIMS) is generally deployed. CIMS is a very sensitive and selective method and detection limits around  $10^5$  molecules of  $\text{H}_2\text{SO}_4$  per  $\text{cm}^3$  and one minute integration time can be reached (Eisele and Tanner, 1993; Young et al., 2008). While most instruments initiate the production of the  $\text{NO}_3^-$  primary ions – which are used for  $\text{H}_2\text{SO}_4$ -CIMS – through the decay of a radioactive substance, these ions can also be generated by a corona discharge. The reason why radioactive ion sources are generally used (usually alpha emitters like Polonium 210 or Americium 241) is probably because these sources are known to be more stable over time and produce cleaner mass spectra, i.e. create lower background concentrations and less interference with other substances like  $\text{SO}_2$ . However, with respect to health risk, cost and meeting safety regulations for shipment, storage and operation, corona ion sources have a clear advantage over their radioactive counterparts.

Corona ion sources for CIMS instruments have been described and used by several groups for the measurement of OH and peroxy radicals (Kukui et al., 2008), other atmospheric trace gases like  $\text{SO}_2$ , acetonitrile and acetone (Jost et al., 2003) as well as  $\text{HNO}_3$  (Furutani and Akimoto, 2002). Using drift-chemical ionization mass spectrometry, corona ion sources have also been deployed for the detection of  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_5$  and isoprene (Zheng et al., 2008; Fortner et al., 2004). Some of the corona ion source-based measurements show a higher complexity as compared to the use of radioactive ion sources (Kukui et al., 2008) while they suffer at the same time from higher detection limits due to radicals produced by the corona discharge (Kukui et al., 2008; Jost et al., 2003). Our findings, however, do not support these observations, something which we relate to the special design of the ion source region and the ion drift tube of the instrument being used in this study.

Here, we describe in detail the set-up of a corona-type ion source and report on its performance when used with a chemical ionization mass spectrometer from THS Instruments (THS Instruments LLC, USA). The results obtained with this ion source are compared to the ones from an americium ion source, a device generally used

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for this type of CIMS measurement. It is demonstrated that the corona ion source works stable and reliably and shows a negligible cross-sensitivity to  $\text{SO}_2$  for sulfuric acid measurements. Most importantly the corona ion source yields almost identical quantitative results as an americium ion source for the same instrument.

## 2 Instrumental description

The corona ion source has been developed for a chemical ionization mass spectrometer from THS Instruments (THS Instruments LLC, USA) for the detection of sulfuric acid. The measurement relies on the reaction between  $\text{NO}_3^-$  primary ions generated in the ion source and sulfuric acid in the sample gas (see Eisele and Tanner, 1993; Berresheim et al., 2000). Originally, we had the instrument equipped with an americium containing thin gold-plated foil (NRD LLC, USA) for providing the primary ions. A schematical drawing of this ion source is shown in Fig. 1. This figure, showing the old set-up, is used to illustrate the working principle of the instrument while the new corona ion source will be introduced and explained in detail further below.

### 2.1 CIMS and americium ion source

The sample gas containing the sulfuric acid is pulled into the ion drift region through a stainless steel tube with an outer diameter of 12.7 mm. It is then exposed to  $\text{NO}_3^-(\text{HNO}_3)_x$  with  $x=0-2$  primary ions which can react with  $\text{H}_2\text{SO}_4$  to form  $\text{HSO}_4^-(\text{HNO}_3)_x$  ions (Eisele and Tanner, 1993; Viggiano et al., 1997). The primary ions in the old set-up originate from the interaction of alpha particles from the radioactive decay of americium ( $^{241}\text{Am}$ ) with the sheath gas. This sheath gas consists of room air cleaned by an activated charcoal as well as by a HEPA filter and has a total flow rate of approximately 22 standard liters per minute (slm). A small amount of  $\text{HNO}_3$  ( $\sim 0.005$  slm of  $\text{N}_2$  saturated with  $\text{HNO}_3$  at room temperature) is added to the sheath gas which leads to the generation of  $\text{NO}_3^-(\text{HNO}_3)_x$  primary ions through a series of

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This feature of our calibration set-up will also be explained in more detail in a separate paper.

The observation that the correspondence between the corona and the americium ion source is nearly perfect is not necessarily expected given the fact that the ions from the corona needle are generated only by a point source whereas for the americium source they are produced over a complete circular cross section (neglecting the small gap between the edges of the americium foil when it is wrapped around the inner cylinder). However, our findings might suggest that space charge distributes the ions homogeneously in the ion drift region. Another, maybe more likely explanation is that even when the primary ions are not homogeneously distributed over the sample gas volume, only  $\text{NO}_3^-$  ions which have been mixed with the sulfuric acid in the sample gas enter the mass spectrometer. Therefore, the ion count rates for  $\text{HSO}_4^-$  and  $\text{NO}_3^-$  are always at a defined ratio for a given  $\text{H}_2\text{SO}_4$  concentration and no  $\text{NO}_3^-$  ions that were not exposed to sulfuric acid in the sample gas are counted. This behavior for the ion collection can be explained by the special design of the interface between the ion drift region and the pinhole plate through which the ions enter the vacuum of the mass spectrometer. In front of the pinhole an electrostatic lens (applied voltage of  $-100\text{ V}$ , see Fig. 1) with an internal diameter that is equal to the one of the sampling tube allows only ions to pass which are close to the centerline. Therefore, primary ions close to the outside wall of the ion drift tube are not detected and do not bias the ratio between analyte and reagent ions.

### 3.2 Signal stability

Figure 4 shows a time series of the signal at  $m/z$  64 over a period of more than two hours. We use  $m/z$  64 ( $\text{NO}_2^{18}\text{O}^-$ ) as our primary ion signal since the count rate at  $m/z$  62 ( $\text{NO}_3^-$ ) can produce a strong signal which might saturate the channeltron detector. The data in the figure shows raw signals with a time resolution of 5 seconds as well as values averaged over one minute. Until 12:57 the background of  $\text{H}_2\text{SO}_4$

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was measured. Then a stable concentration of  $\text{H}_2\text{SO}_4$  was produced in our calibration set-up. The signal of the primary ion shows some fluctuations and a small drift can be identified with a slightly increasing ion count rate over time. These changes were not observed as strongly with the americium ion source and we attribute the higher “noise” of the corona ion source to changes in the corona onset voltage which might occur due to temperature changes or slight changes in the sheath gas composition (humidity). However, these changes are rather small and slow. In addition, since  $[\text{H}_2\text{SO}_4]$  is proportional to the ratio of the count rates at  $m/z$  97 and  $m/z$  64 these drifts do not show up in the  $\text{H}_2\text{SO}_4$  signal. Over longer time scales of up to weeks the count rate of the primary ion signal stays within  $\pm 50\%$ . This means that the same corona needle can be used for rather long times and that no observable limitation on the detection limits is occurring.

### 3.3 Cross-sensitivity to $\text{SO}_2$ and detection limit

The dependence of the  $\text{H}_2\text{SO}_4$  measurement on the  $\text{SO}_2$  concentration is also shown in Fig. 4. At 12:30 a concentration of 1 ppmv of  $\text{SO}_2$  was introduced into the sample gas while no  $\text{SO}_2$  had been actively introduced before. The average  $\text{H}_2\text{SO}_4$  concentration increases from  $2.9 \times 10^4$  to  $\sim 6.1 \times 10^4 \text{ cm}^{-3}$  due to the higher  $\text{SO}_2$  concentration. When taking into account the point to point fluctuations for the signals, detection limits (based on the averaged one minute values plus three times their standard deviation) of  $6.4 \times 10^4 \text{ cm}^{-3}$  and  $1.1 \times 10^5 \text{ cm}^{-3}$  are obtained for the periods without and with the addition of  $\text{SO}_2$ , respectively. Even the higher value is still better than what has been reported from another group for a similar CIMS with a polonium ion source (Young et al., 2008).

The concentration of sulfur dioxide which was added for the example shown here is large in comparison to concentrations usually observed at ambient conditions even in moderately or strongly polluted cities (Bari et al., 2003; Yang et al., 2009). Considering the large amount of  $\text{SO}_2$  added to the sample gas, a twofold increase in the background  $\text{H}_2\text{SO}_4$  seems to be a negligible contribution and indeed, no cross-sensitivity to  $\text{SO}_2$

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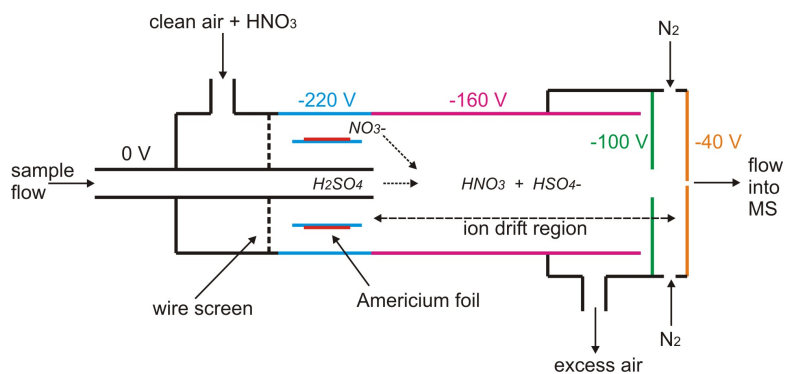


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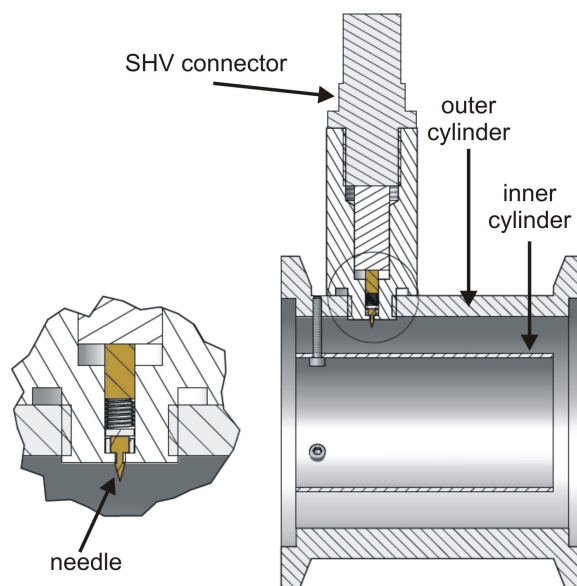
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**Fig. 1.** Schematic drawing of the ion source and the inlet system of the instrument used for the  $H_2SO_4$  measurements. The colors represent different voltages applied to the different sections of the inlet and ion source region. Note that the voltage applied to the americium foil is  $-220\text{ V}$  as well but has been assigned a different color for clarity.

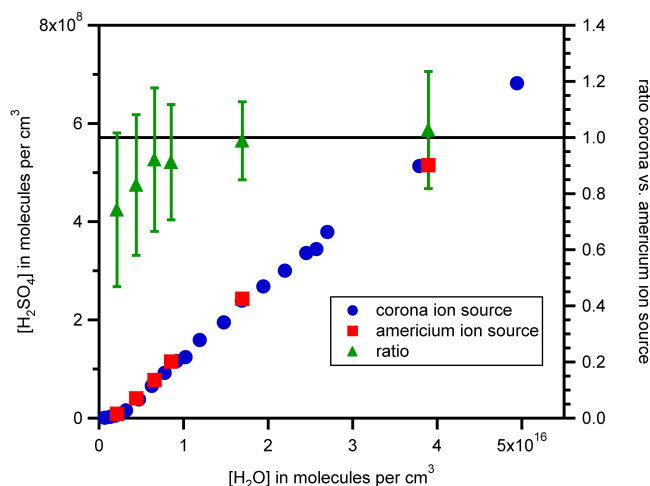
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**Fig. 2.** Technical drawing of the new corona ion source set-up. The section on the left shows the magnified corona needle (in gold) and the compression spring which establishes the electrical contact to the SHV feedthrough. Direction of flows is from left to right.

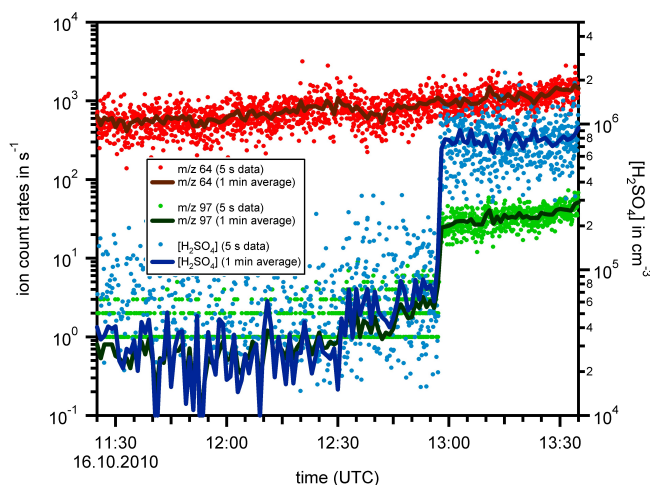
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**Fig. 3.** Measured H<sub>2</sub>SO<sub>4</sub> concentrations when operating the CIMS instrument with an americium and with a corona ion source, respectively. Different H<sub>2</sub>SO<sub>4</sub> concentrations were adjusted by a calibration system. These are a function of [H<sub>2</sub>O] shown on the x-axis. Error bars for the H<sub>2</sub>SO<sub>4</sub> values have been neglected for clarity. The main error for the ratios between the values for the corona and the americium ion source comes from the uncertainty in the temperature measurement (which is assumed to be ±1 °C). This error in temperature affects the conversion from relative humidity into concentration of H<sub>2</sub>O strongly due to the dependence of the water vapor saturation pressure on temperature.

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**Fig. 4.** Time series of the primary ion signal NO<sub>2</sub><sup>18</sup>O<sup>-</sup> (*m/z* 64), the HSO<sub>4</sub><sup>-</sup> ion (*m/z* 97) and the derived H<sub>2</sub>SO<sub>4</sub> concentrations from the signals. SO<sub>2</sub> at 1 ppmv was introduced into the sample gas at 12:30; H<sub>2</sub>SO<sub>4</sub> was generated around 12:57 with a calibration set-up external to the CIMS instrument.

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