

**Appendix C:**  
**Effect of Relative Humidity on the Detection of Sulfur Dioxide  
and Sulfuric Acid Using a Chemical Ionization Mass  
Spectrometer\***

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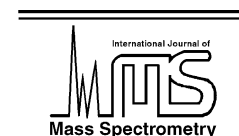
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## Effect of relative humidity on the detection of sulfur dioxide and sulfuric acid using a chemical ionization mass spectrometer

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### Abstract

Detection of sulfur dioxide and sulfuric acid at high relative humidity was studied using a chemical ionization mass spectrometer (CIMS). The reactant ions used in the experiments are  $\text{CO}_3^- \cdot n\text{H}_2\text{O}$  ( $n = 0-5$ ), which react with  $\text{SO}_2$  to form  $\text{SO}_5^- \cdot n\text{H}_2\text{O}$  ( $n = 0-2$ ).  $\text{H}_2\text{SO}_4$  reacts with the precursor ions to form  $\text{HSO}_4^-$  ( $m/z = 97$  amu) and  $\text{H}_2\text{SO}_4 \cdot \text{CO}_3^-$  ( $m/z = 158$  amu). We report the first use of the latter ionization scheme to detect sulfuric acid. High RH affects the detection of  $\text{SO}_2$  and  $\text{H}_2\text{SO}_4$  by forming clusters with the reactant and product ions, reducing sensitivity. Increasing the temperature breaks these clusters. For  $\text{SO}_2$  at high RH, either  $\text{SO}_5^-$  ( $m/z = 112$  amu) or  $\text{SO}_5^- \cdot \text{H}_2\text{O}$  ( $m/z = 130$  amu) can be used for  $\text{SO}_2$  detection without a decrease in sensitivity. For  $\text{H}_2\text{SO}_4$  at high RH, it is preferred to detect the ion  $\text{H}_2\text{SO}_4 \cdot \text{CO}_3^-$  because the background signal at 158 amu is small, and a better sensitivity can be achieved.

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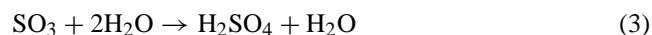
**Keywords:** Chemical ionization mass spectrometer; Sulfur dioxide; Sulfuric acid; Water clusters; Relative humidity

### 1. Introduction

The predominant anthropogenic sulfur-containing compound directly emitted into the atmosphere is sulfur dioxide, the atmospheric oxidation of which produces sulfuric acid [1]. Sulfuric acid has been implicated in the formation of new particles in the atmosphere through nucleation in combination with water and possibly ammonia [2], and it can also promote the growth of pre-existing particles by condensation on their surfaces. Once these particles reach a few hundred nanometers in diameter they might have a significant impact on the formation of clouds and regulation of global climate through efficient scattering of sunlight [3].

$\text{SO}_2$  is emitted predominantly through fossil fuel combustion and is also a major oxidation product of reduced sulfur compounds in the atmosphere, such as dimethyl sulfide (DMS) [1]. Mixing ratios of sulfur dioxide in continental background air range from 20 ppt to over 1 ppb. In the unpolluted marine boundary layer levels range between 20 and 50 ppt. Urban  $\text{SO}_2$  mixing ratios can attain values of several hundred parts per billion [4].

Sulfuric acid vapor in the atmosphere is mainly a product of the gas-phase oxidation of  $\text{SO}_2$  by the hydroxyl (OH) radical [5,6]:



Field measurements show a strong diurnal variation in  $\text{H}_2\text{SO}_4$  tracking the UV solar flux, which drives the formation of OH. Since  $\text{H}_2\text{SO}_4$  has a very low vapor pressure (below  $10^{-12}$  atm [7]), once formed, it tends to condense

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