

# Using chemical ionization mass spectrometry for detection of HNO<sub>3</sub>, HCl, and ClONO<sub>2</sub> in the atmosphere

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## Abstract

Ion chemistry schemes involving three different reagent ions are described for measuring nitric acid (HNO<sub>3</sub>), hydrochloric acid (HCl), and chlorine nitrate (ClONO<sub>2</sub>) in the upper troposphere and lower stratosphere using chemical ionization mass spectrometry (CIMS). These schemes were evaluated in the laboratory for sensitivity and selectivity of the neutral species. The use of one scheme, based on the SF<sub>5</sub><sup>-</sup> reagent ion, is described for airborne measurements. Initial atmospheric measurements show that HNO<sub>3</sub>, HCl, and ClONO<sub>2</sub> can be measured using SF<sub>5</sub><sup>-</sup> with high precision and accuracy.

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## 1. Introduction

Chemical ionization mass spectrometry (CIMS) has been used as a sensitive measure of nitric acid (HNO<sub>3</sub>) and a number of other trace species in the atmosphere [1–16]. Quantification of many of these species in the atmosphere is of interest for our understanding of homogeneous and heterogeneous chemical and physical processes. Measurement of some trace species such as hydrochloric acid (HCl) and chlorine nitrate (ClONO<sub>2</sub>) are also of interest because these molecules can be useful as tracers of stratospheric air masses and stratospheric ozone that have penetrated into the upper troposphere [1]. More detailed knowledge of HCl and ClONO<sub>2</sub> concentrations in the lower stratosphere will also lead to a better understanding of the stratospheric chlorine budget because both are principal reservoirs of inorganic chlorine [17,18].

The CIMS technique ideally employs reagent ions that react selectively with the trace species of interest to produce a unique product ion, with minimal interference from other re-

actions. Measurement of the product ion is then used to quantify the abundance of the trace gas in the atmosphere. Reactions of many reagent ions with HNO<sub>3</sub>, HCl, and ClONO<sub>2</sub>, as well as other atmospheric trace gases, have been studied in the laboratory for the expressed purpose of using the reactions for atmospheric CIMS measurements [2–4,19–23]. In addition, several of these reactions have been used to make measurements of these three species in the atmosphere. For example, CIMS instruments have been used to measure atmospheric HNO<sub>3</sub> using SiF<sub>5</sub><sup>-</sup> as the reagent ion and HNO<sub>3</sub>·SiF<sub>5</sub><sup>-</sup> as the product ion [2,5–9]. The yield of HNO<sub>3</sub>·SiF<sub>5</sub><sup>-</sup> is proportional to the amount of HNO<sub>3</sub> in the sample and is calibrated by adding a known amount of HNO<sub>3</sub> to the instrument from a permeation tube source [5]. HNO<sub>3</sub> has also been measured in the atmosphere using Cl<sub>n</sub><sup>-</sup> or CO<sub>3</sub><sup>-</sup> reagent ions [10–13]. HCl can be detected by CIMS using the reagent ions NO<sub>3</sub><sup>-</sup>·H<sub>2</sub>O, CF<sub>3</sub>O<sup>-</sup>, and SF<sub>5</sub><sup>-</sup> [1,3,14,24]. A fluoride transfer from CF<sub>3</sub>O<sup>-</sup> or SF<sub>5</sub><sup>-</sup> to HCl produces the product ion HFCl<sup>-</sup>. CF<sub>3</sub>O<sup>-</sup> has also been shown to react with ClONO<sub>2</sub> by fluoride transfer [21]. In the present study, we have investigated three reagent ions (SF<sub>5</sub><sup>-</sup>, CF<sub>3</sub>O<sup>-</sup>, and CH<sub>3</sub>SiF<sub>4</sub><sup>-</sup>) in the laboratory and evaluated their suitability for use in the

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measurement of  $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{ClONO}_2$  in the atmosphere. We show that, in addition to previously demonstrated reactions, the reagent ion  $\text{CH}_3\text{SiF}_4^-$  reacts via fluoride transfer to  $\text{HCl}$  and that  $\text{SF}_5^-$  transfers fluoride to  $\text{ClONO}_2$ . On the basis of the laboratory work, the  $\text{SF}_5^-$  reagent ion was determined to be the best candidate for use in atmospheric measurements of  $\text{HCl}$  and  $\text{HNO}_3$ , and is suitable for measurement of  $\text{ClONO}_2$ , which is a secondary objective of the airborne studies. The  $\text{SF}_5^-$  ion was used in flight in the NOAA airborne CIMS instrument during the NASA Cirrus Regional Study of Tropical Anvils and Cirrus Layers–Florida Area Cirrus Experiment (CRYSTAL–FACE) mission in July 2002. During this mission,  $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{ClONO}_2$  were measured in the upper troposphere and lower stratosphere (UT/LS).

## 2. Laboratory studies

The primary objective of the laboratory tests was to establish whether any of the reagent ions was suitable for use in airborne CIMS measurements of  $\text{HCl}$  or  $\text{HNO}_3$  in the UT/LS. The criteria for suitability includes (i) no significant detection interference for the product ion from contaminant ions of the same, or nearly the same mass, (ii) a well defined relationship between the measured product ion count rates and the concentrations of the species measured, and (iii) no significant reactive interference from the presence of other atmospheric species, such as ozone or water.

The laboratory studies were conducted with a CIMS instrument that is functionally equivalent to the flight instrument, which has been described in detail elsewhere [5]. The laboratory instrument is arranged in a configuration that allows relative ease of operation and modification. As diagrammed in Fig. 1, the instrument has a 35 cm long and 5 cm diameter flow tube. A 2 standard liter per minute (slm) flow of  $\text{N}_2$  carries the reagent ion precursor gas through a commercial

$^{210}\text{Po}$  radioactive source (NRD Incorporated, Grand Island, NY) [5,6] where the reagent ions are produced. This source is a 20 mCi alpha emitter that produces secondary electrons in the primarily nitrogen flow, which then attaches to the reagent ion precursor molecules to give the reagent ions. The reagent ion flow enters on the opposite side of the flow tube entrance from the “sample” flow. In the laboratory, the sample is a flow of 2 slm dry  $\text{N}_2$  rather than an inlet flow from the atmosphere as used in the flight instrument. Known amounts of  $\text{HCl}$  from a standard bottle or  $\text{HNO}_3$  from a permeation tube can be added to the laboratory sample line to determine sensitivities and detection limits for each of the reagent ions. The laboratory flow tube is operated at room temperature and maintained at a pressure of 22 hPa by a scroll pump when the total flow is 4 slm. The size of the flow tube and the pressure, temperature, and rate of gas flow result in a residence or reaction time in the flow tube of 0.18 s. At the downstream end of the flow tube, ions pass into a quadrupole mass spectrometer through a 0.5 mm diameter aperture. The quadrupole chamber is pumped to 0.01 Pa by two turbo-molecular pumps. The spectrometer can either be scanned through a range of masses, or set to monitor a single mass for a given period of time. The ions that are transmitted through the quadrupole are detected by a Channeltron-type electron multiplier (Detector Technology, Palmer, MA) in a chamber pumped to  $10^{-3}$  Pa by a third turbo-molecular pump.

### 2.1. Reagent ion options

The reagent ion  $\text{SF}_5^-$  is produced from trifluoromethyl sulfur pentafluoride ( $\text{SCF}_8$ , Apollo Scientific, UK). Electron attachment to  $\text{SCF}_8$  in the  $^{210}\text{Po}$  source in the CIMS instrument primarily produces  $\text{SF}_5^-$  [25,26]. ( $\text{SCF}_8$  has been detected in the atmosphere at concentrations of 0.12 parts per trillion by volume (pptv) [27]. It is thought to be produced in  $\text{SF}_6$ -gas-insulated high voltage equipment that contains flu-

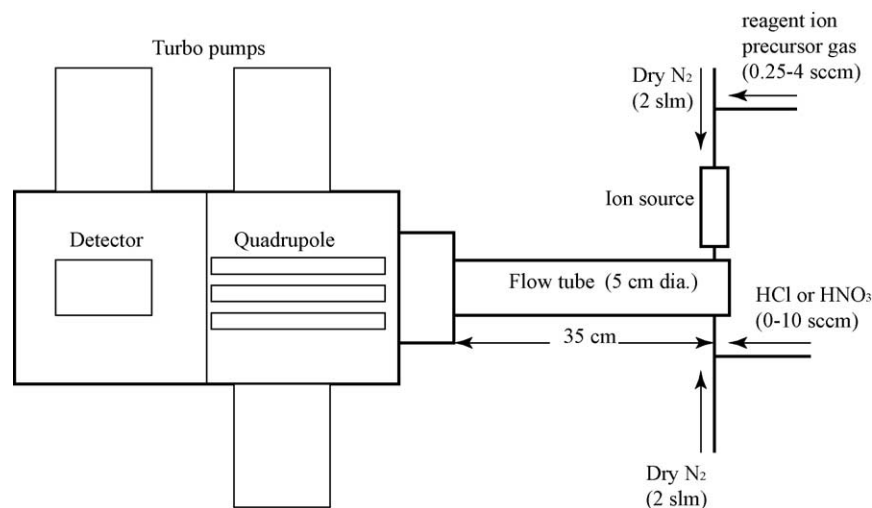


Fig. 1. Schematic of the laboratory CIMS instrument. Flow tube pressure = 22 hPa and residence time = 0.18 s. Reagent precursor gas flow ranges from 0.25 to 4.0 sccm depending on the gas being used.

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