

Determination of ultra-trace amount of halo-hydrocarbon in nitrogen by atmospheric pressure ionization mass spectrometry

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Abstract. The monitoring of halo hydrocarbons such as R134a in atmosphere has attract great attention due to its strong global warming effect. In this study, on-line atmospheric pressure ionization (API) and electron impact ionization (EI) mass spectroscopy was used to measure R134a at ambient level (ppt, 10^{-12} mol/mol). A dilution system was developed to test the linearity of API/EI MS. Results showed that the sensitivity of API MS was much higher than that of EI MS. A good linearity could be obtained at the range of 10-75 ppt for API MS. The API MS could directly measure R134a at ambient level without preconcentration devices.

Introduction

The growing concern of global warming and ozone depletion will require long term monitoring of trace atmospheric substance linked to these issues. 1,1,1,2-tetrafluoroethane (R134a) have been used as the major surrogate for refrigerating substance due to its low impact on the ozone layer compared with dichlorodifluoromethane (R12) and trichlorofluoromethane (R11) [1]. However, the long term impact of R134a on the global warming still needs further investigation. Thus, the precise measurement of R134a is important.

However, the precise measurement of R134a is a challenging task. The mole fractions of these compounds are usually part per trillion (ppt, 10^{-12} mol/mol), which is lower than the detection limits of the traditional ECD or FID [2]. Cryogenic preconcentration devices could be used to improve the instrument sensitivity. Nevertheless, there is a need for continuous supply of liquid nitrogen or liquid argon in such device. This makes the measurement at remote field location difficult. Besides, the adsorption and desorption process is time consuming, leading a low temporal resolution for the measurement. A direct measurement of R134a without preconcentration could be helpful to improve efficiency of atmospheric monitoring. In this study, an on-line atmospheric pressure ionization mass spectroscopy (API MS) is developed. This API MS is optimized to measure R134 at ppt level without preconcentration.

Materials and Methods

The R134a standard gas mixtures were prepared by the gravimetric method [3]. A small cylinder was used as the intermediate vessel to transfer the small amount of gas into the target cylinder (Figure 1). Before gas mixture preparation, both the target cylinder and the small cylinder was vacuumed by turbo-molecular pump (Pfeiffer, Germany) to clean the inner wall of cylinder. A certain amount of Pure R134a was filled into the small cylinder. Then, the small cylinder was connected with target cylinder to transfer the pure R134a into target cylinder. The mass of gas transferred into the target cylinder was determined by the weight loss of the small cylinder. A mass comparator (Mettler, Switzerland) was used to measure the gas mass.

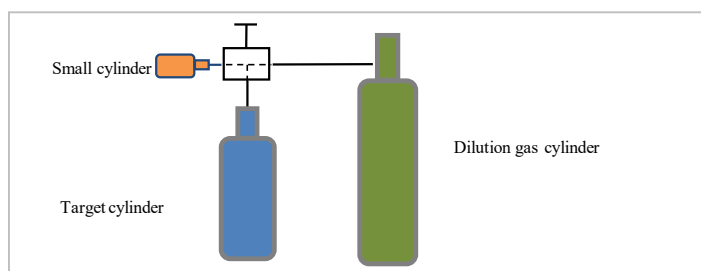


Figure 1: Preparation of gas standard mixture using a small cylinder

The R134a standard gas mixture was introduced into online mass spectrum (API/EI MS) through a dilution system. The original R134a standard gas mixture was diluted by purified nitrogen. The dilution ratio was controlled by two thermal mass flowmeter (MFC, Horiba, Japan). A gas purifier was used to remove the moisture in nitrogen (Figure 2). The gas mixture was homogenized in the mixing chamber at a constant temperature of 50 °C and then introduced into the MS.

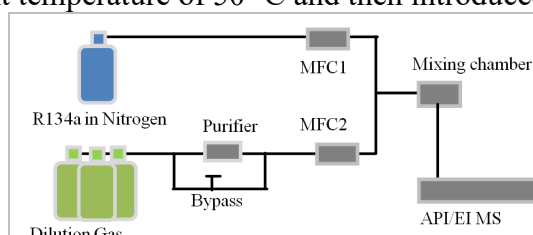


Figure 2: Schematic view of experiment set-up

Figure 3 is the configuration of API/EI MS. This online mass spectrum is equipped with two ion source (Extrel, USA). One is atmospheric pressure ion source (API), and the other is electron impact ion source (EI). The switch of these two ion source could easily be done by turning on of one power source while turning off the other. A purge flow rate of 2 L/min-5 L/min is recommended for keeping the background cleanness.

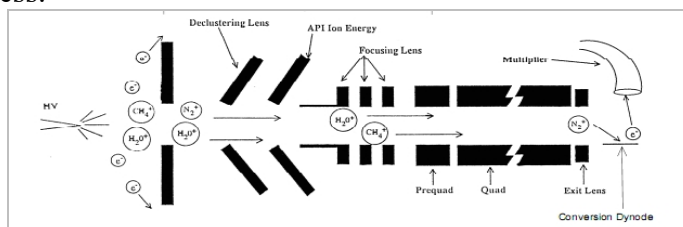
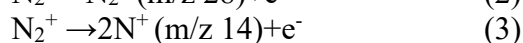
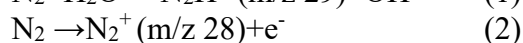
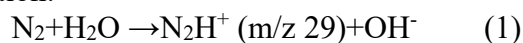


Figure 3: Configuration of API/EI-MS

Under API model, the sample gas was ionized under atmosphere pressure. The ion was guided into the mass analyzer through a 25µm orifice. The number of ions that can be introduced through the orifice determines the sensitivity of the API MS. The ions were separated by a series of focusing lens and a radio frequency quadrupole before they reach the mass analyzer.

The effect of moisture on API/EI MS

The moisture had a great impact on ion detected by API/EI MS. The moisture may come from carry gas and water molecular desorbed from inner wall of sampling line. The moisture concentration at the end of the sampling line was measured by a moisture meter (Delta-F, USA). Result showed that long purging time was needed to remove the background moisture in sampling line. The moisture concentration was about 0.51ppm after 5min purging and could be further reduce to 270 ppt after 72h purging. Figure 1 showed that the nitrogen ion detected by MS varied with purging time. At 5mins, the m/z peak of 29 showed that N₂ H⁺ was formed through reaction (1). After 72h purging, the peak intensity of 29 was greatly reduced, showing the moisture concentration had an impact on ion speciation.



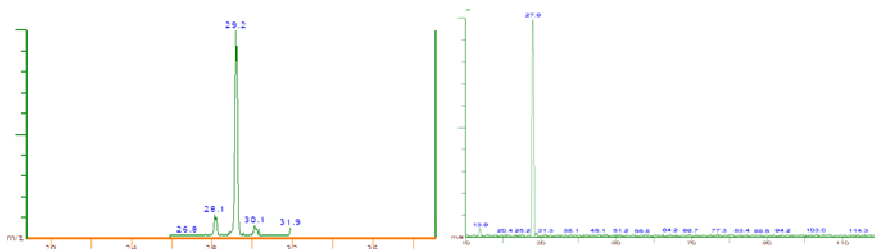


Figure 4: The effect of moisture on N₂⁺ and N₂H⁺ speciation

The chosen of quantification ion

After purging the sample line for 72hrs, both the back ground noise and response factor reached a steady state. Then, serials of diluted gas standards were introduced to test the linearity range of the MS. Both electron impact ionization (EI) and atmospheric pressure ionization (API) were used as ionization sources. The MS was carefully tuned to balance the sensitivity and linearity before the test. According to the standard spectrum of R134a in NIST library, m/z 51, m/z 63, m/z 69 and m/z 83 were all fragment ions originated from R134a (Figure 4). The ion at m/z 69 was chosen as the quantification ion due to the low interference near m/z 69.

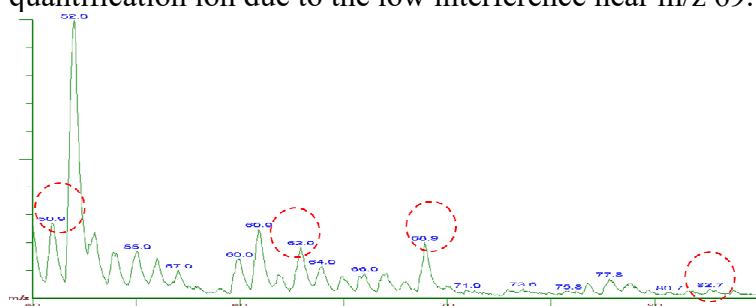


Figure 5: The EI-MS spectrum of 0.5ppm R134a in N₂

The linearity range of API/EI MS

Results showed that the linearity range for API source was much lower than EI sources. The linearity range was about 75-600 ppb for EI source, while the linearity range is about 10-75ppt for API sources (Figure 5 and Figure 6). There was also great sensitivity difference when instrument was switch between API source and EI source. The sensitivity of API MS was much higher than EI MS. The limit of detection (LOD) of EI MS was about 70 ppb, while LOD of API MS was about 8 ppt.

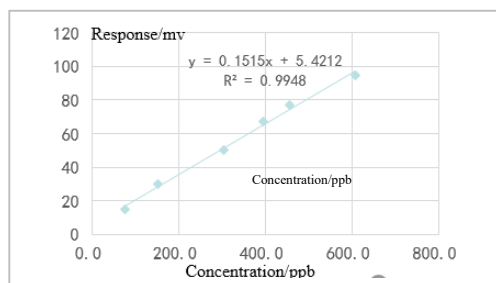


Figure 6: The linearity range of EI MS

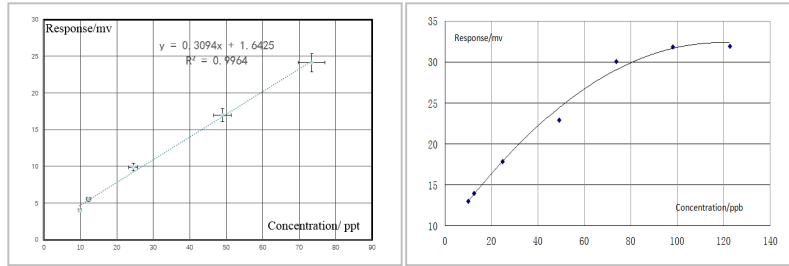


Figure 7: The linearity range of API MS

Acknowledgements

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