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RESEARCH PAPER

Determination of Gaseous and Particulate Trifluoroacetic Acid in Atmosphere Environmental Samples by Gas Chromatography-Mass Spectrometry

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Abstract: Trifluoroacetic acid (TFA) were determined in air samples by a sampling device composed of annular denuders coupled with a quartz filter, which was efficient for the collection and separation of gaseous and particulate TFA. Gaseous TFA was performed by means of annular denuders coated with alkaline solution, while particulate TFA was absorbed by quartz filters. TFA can be determined by gas chromatography-mass spectrometer after derivatizated with 2,4-difluoroaniline. Calibration curves were linear with correlation coefficients of 0.9991. Detection limit of TFA was 66 ng L^{-1}, which was 31 pg m^{-3} when sampling volume was 48 m^3. Recoveries of the TFA sampling device ranged from 98% to 105% with relative standard deviation (RSD) $\leq$ 3%. The developed method was applied to the determination of TFA in atmosphere samples collected in Peking University in Beijing in 2012. Total TFA concentrations ranged from 501 to 7447 pg m^{-3}. Concentrations of gaseous TFA were significantly higher than those of particulate, and the gas-particle partition coefficient of TFA decreased as air temperature rose.

Key Words: Trifluoroacetic acid; Annular denuder; Sampling; Gas chromatography-mass spectrometry; Gas-particles partition coefficient

1 Introduction

Some alternative products have been developed to substitute CFCs (Chloro-fluoro-carbon) such as 1,1,1,2-Tetrafluoroethane (HFC-134a), 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123) and 1-chloro-1,2,2,2-tetrafluoroethane (HCFC-124) which can be oxidized and degraded to trifluoroacetic acid (TFA)[1,2]. TFA can also be generated by pyrolysis of fluorine-containing polymer[3,4]. In China, HFC-134a is widely used as the refrigerant, and it is expected that the annual demand of HFC-134a will reach 35,000 tons by 2015 only in the automotive air conditioning industry[5]. Production of PTFE reached 65000 tons in 2010 with an annual growth rate of over 25%. Production and consumption of fluoride will cause a rapid increase of TFA in the environment.

TFA is a typical fluorinated organic acid. When the TFA finally deposited and accumulated in water body, it would affect the aquatic plants by restraining plants growing in water body, and the human body was poisoned exposed to the TFA concentration of 250 μg L^{-1} for 2 h[6]. Particularly, TFA is not likely to be degraded through chemical reaction or microorganism degradation in water and along with the increasing potential sources of TFA, TFA will accumulate to a certain concentration in water bodies, which endangers the ecological environment and human health.

At present, the studies on TFA was focused on the determination of its concentration in water body[7–10], while the study on the concentration of TFA in the atmosphere was not common[11–15]. Since TFA is mainly produced by fluorochemicals reactions in the atmosphere, the determination of TFA in atmospheric is necessary and urgent

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to evaluate the impact of HFC-134a and other fluorine-containing material on the ecological environment. In this experiment, the TFA in air samples were collected by a sampling device composed of annular denuders coupled with a quartz filter, which was efficient for collection and separation of gaseous and particulate TFA. After derivatizated with 2,4-difluoroaniline, TFA can be determined by gas chromatography-mass spectrometry. A high collection efficiency of the sampling was obtained to overcome the gas phase interaction of the particles. By this method, the synchronous sampling-separation of TFA was carried out for the study of the phase distribution in the atmosphere. The optimization of conditions for TFA derivatization improves the detection sensitivity.

2 Experimental

2.1 Instruments and reagents

2000-ø 30 mm × 242 mm-3CSS annular denuders and 2000-02 AB pump were obtained from American URG Company, USA. QP-1000 SE GC/MS (Shimadzu Company, Japan), DB-17 capillary column (30 m × 0.32 mm × 0.25 μm, Agilent Company, USA), N-1100S-W type EYE-LA rotary evaporator (Tokyo Rikakikai Co. Ltd., Japan) and THZ-C constant temperature oscillator (China Nantong Company, China) were used in this study.

Perfluoropropionic acid (PFPA) and trifluroacetic acid (99%) were purchased from Acros Organics Company, Belgium. *N*,*N*-dicyclohexylcarbodiimide (DCC, ≥ 99.0%) was obtained from Switzerland Fluka Company. 2,4-Difluoroaniline (≥ 99.0%) was obtained from American J&K Chemicals Company.

A coating solution was prepared by mixing 1% Na_2CO_3 solution and 1% glycerol-methanol solution in a proportion of 1:1 (*V/V*) and then stored in refrigerator in reserve. Quartz filters were baked at 450 ºC for 6 h, and then packed by aluminum foil paper in sealing bag.

2.2 Sampling

2.2.1 Cleaning and coating of denuders

Denuders were washed with secondary distilled water, acetone, hexane respectively, and then dried under a flow of high-purity nitrogen (99.999%). After sealed one end, a 10 mL mixed solution of sodium carbonate-water/glycerol-methanol solution abovementioned was poured into the dry denuders to coat the internal walls of the dry denuders. After the other end was also sealed, the denuders were shaken for 1 min, and then the excess solution was decanted. The wet denuders were dried under a flow of high-purity nitrogen, and sealed before use. Weigh it before and after use.

2.2.2 Installation of sampling apparatus

The apparatus in this experiment was an automatic speed-controlling air sampling device that consisted of five parts: cyclone inlet (2.5 μm cut), glass annular denuders, QM-A quartz fiber filters, mass flow controller and pump. Keep The denuders were kept in series and fixed vertically. The whole equipments were placed in a vertically stationed sampling box whose inner temperature was higher than that of ambient by 2 °C to minimize the condensation of water vapor.

2.2.3 Sampling location and conditions

The sampling site was on the roof of Science Building at Peking University. The air inlet diameter of apparatus was 4.00 mm. In order to effectively separate $PM_{2.5}$, air flow rate was set to 16.7 L min^{-1} [16]. The sampling time was lasted for 48 h and the total volume was 48 m^3.

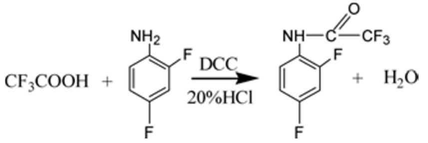
2.2.4 Sample extraction

For each gaseous sample, the coating with TFA was extracted three times by secondary distilled water (10, 10 and 5 mL).

For particle phase samples, the quartz filters with TFA were cut into small pieces and then immersed in 15 and 8 mL secondary distilled water. After extracted by ultrasonic vibration for 30 min, the mixture above was filtered by aqueous filtration (ø 22–0. 45 μm) and the quartz filters pieces were rinsed with 2 mL distilled water. The combined extraction was prepared for the analysis of the concentration of particulate TFA.

2.3 Derivatization and purification of samples

TFA could not be directly determined. In this study, 2,4-difluoroline was used to derive acid anilide from TFA through derivatization reaction. The product was analyzed by gas chromatography with mass selective detector (GC-MS). The equation is as follows:



(1)

Approximately 8 μL PFPA of 15.7 mg L^{-1} was added into a 25-mL extracted solution (of denuders or filters) as internal standard (pH 1, adjusted by 20% HCl). Then 15 mL ethyl acetate, 10 μL 2,4-DFAn, 40 μL DCC and 1.0 g NaCl were added into the solution in turn. The obtained mixture above was oscillated for 1 h at 35 ºC and by this way, the TFA in the sample will transfer to the ethyl acetate phase. After still stratification, the separated ethyl acetate phase was kept. Another 5 mL ethyl acetate and 0.5 g NaCl was added into the