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Monitoring of trifluoroacetic acid concentration in environmental waters in China

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Abstract

It is critically important and extremely meaningful to determine the concentration of TFA in the environmental water in China. This will create background reference for the effects of analyzing the extensive employment of the substitutes to CFCs in China. In this paper a set of analytical methods was described for use in monitoring of trifluoroacetic acid (TFA) concentration of environmental waters including collecting, pre-treatment measures, preserving, concentrating and derivatization of samples from different kinds of environmental waters. The GC with electrical capture detector (ECD) and headspace auto sampler were used in the analysis. The lowest detection limit of the instrument is 0.0004 ng methyl trifluoroacetic acid (MTFA), and the lowest detected concentration with the method is 3.0 ng/ml TFA. TFA collected in various environmental water samples (including rainfall, inland surface water, ground water, and waste water) from nine provinces and autonomous regions in China have been determined by applying the analytical methods created and defined in this work. The results indicate that the concentrations of TFA in nine rainfalls and three snowfalls through the period from 2000 to 2001 ranged from 25 to 220 ng/l, the TFA concentration in the inland surface water samples ranged from 4.7 to 221 ng/l, the concentration of TFA in groundwater samples collected in Beijing was 10 ng/l, and the TFA concentration in coastal water samples ranged from 4.2 to 190.1 ng/l.

Keywords: TFA; Collecting; Environmental waters; Determine

1. Introduction

Currently, for their destroying effect on ozonosphere, the production and use of ozone-depleting substances (ODS), such as chlorofluorocarbons (CFCs) are controlled strictly in global range; at the same time, some alternative products have been developed to substitute CFCs to satisfy the increasing demands of people in production and living conditions (McCulloch, 1999), among which HFC-134a, HCFC-124 and HCFC-123 are widely used. However, these alternatives can react with OH free radical in atmosphere (Tromp, 1995), and then degraded to trifluoroacetic acid (TFA, CF_3COOH) which could arrive on the ground by means of dry or wet deposition (Wallington et al., 1996). If rain washout was the only removal mechanism of TFA, it is predicted that, by 2010, the average concentration of TFA in global rain will go up to 0.16 μg/l (Tromp, 1995).

Trichloroacetic acid (CCl_3COOH), the same category substance as TFA, is known as a carcinogen, which arouses wide concerns on TFA on its formation mechanism and health effect (Tromp, 1993). Atmospheric TFA is removed mainly by rain washout, and only 10–20% of it reacts with OH free radical

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(Møgelberg et al., 1994), then CF_3 and CO_2 will be generated with the breaking of C–C bond in TFA. In atmosphere, the life of TFA is around 5–15 days (Wallington et al., 1994); when TFA finally deposited and accumulated in soil and water body, and when it is not likely to be degraded through chemical reaction or microorganism degradation, it will affect the ecosystem by restraining plants growing in water body as TFA concentration comes up to 100–300 ng/l.

Ole John Nielsen etc. (Nielsen et al., 2001) have collected five fresh water samples that created before the industrialization period (2000 years ago) from ice core of Greenland and old groundwater in Denmark, and no TFA was detected in either of them (<2 ng/l). Based on available data, TFA is not one naturally-generated trace content in fresh water environment.

According to the *National Plan for Phasing out Ozone-Depleting Substances in China* framed by State Environmental Protection Administration of China, China will eliminate CFCs completely by 2010, as a result, the production and use of their alternatives such as HCFCs and HFCs will rise up, and the potential source of TFA is gradually increasing. Therefore, currently, it is important to monitor and analyze TFA in environmental media such as atmosphere, water body (including fresh water and sea), and soil, to obtain TFA concentrations, which plays a key role for environmental assessment and policy framing on alternative products of CFCs in China.

So far, basic data about TFA concentration in environmental media in China are still unavailable. In this study, analysis method for TFA is established, and TFA concentrations are determined in some rivers and lakes, seas and rainwater in China.

2. Experiment

2.1. Materials and equipments

Trifluoroacetic acid (TFA), is bought from Beijing Institute of Science and Technology; Methyl trifluoroacetic acid (MTFA) is bought from Aldrich Chemical Company. Derivatization reagent, dimethyl sulfate (DMS, AR) is purchased from Beijing Changping Shiying Chemical Inc.

Instruments in the analytic system include SHIMADZU GC-14B gas chromatogram, SHIMADZU electrical capture detector (ECD), SHIMADZU HS-2B Headspace auto sampler and bottle, PTFE bottle mat and specific aluminum seal cover; chromatogram column is Supel plot Q capillary column of 30 m in length and 0.32 mm inside diameter, and its highest working temperature is 250 °C. Rotary Evaporator is purchased from YAMATO Inc. Once-off sampler and sampling head are purchased from Chaitian Industrial Machine Inc. Seal film is bought from American National Can, USA, and water sampler (1000 ml) is purchased from SIBATA company, Japan.

2.2. Methodology

TFA cannot be analyzed and determined directly by chromatogram. In strong acid media, nucleophilic substitution reaction occurs between CF_3COO and dimethyl sulfate (DMS). TFA will fully ionize in sulfate media, then reacts esterifiably with DMS with high speed, and produce Methyl trifluoroacetic acid (MTFA) which can be determined by GC-MS quantitatively. The solubility of MTFA in strong acidic media is low, and the volatility of MTFA is high (boiling point 43 °C). In the temperature of 45 °C, the reaction can reach equilibrium, and MTFA can be concentrated and analyzed through headspace injector.

$$\begin{array}{ccc} CF_3COO^- + (CH_3)_2SO_4 & \rightarrow & CF_3COOCH_3 + CH_3SO_4^- \\ H_2O \downarrow & & \downarrow H_2O \\ CH_3OH + H(CH_3)SO_4 & & CF_3COOH + CH_3OH \end{array}$$

Headspace sampling analysis is a method determining concentration of the compound of liquid sample by determining the compound content of vapor over the sample, which is an indirect analysis method based on distribution equilibrium of the compound between gas and coacervate (liquid or solid). Therefore, the content of gas could suggest that of the coacervate. Headspace analysis is an extraction process of the compound by air, which can purify the sample by using the gas as "solvent" to extract the volatile content in the samples. TFA quantitative analysis system using Headspace-Gas chromatogram-ECD detector (HS-GC-ECD) was established in this experiment (Zehavi and Seiber, 1996; Zhang et al., 2001).

2.3. Sampling and treatment

2.3.1. Sampling

In selecting sampling sites, different kinds of water bodies and different regions in China are fully considered with the purpose of obtaining samples which can reflect the current TFA level in environmental water in China (see Fig. 1 for the sampling sites). The concentration of TFA in environmental water is quite low, and the scope of sampling sites are large, moreover, TFA samples are easily polluted; therefore, all samples should be sealed properly during the collection, transportation and storage, and the environment around samples should keep clean and far away from sample treatment lab and analysis lab in order to avoid occurring intercrossing pollution.

All sampling containers must be cleaned by tap water before being used, then be cleaned in ultrasonic liquid