Effect of humidity on atmospheric VOCs measurement

Zhe Bi¹, Yaolong Shi², Zhen Wang¹, Xiao Han¹ and Man Wang¹

¹ Environmental Metrology Centre, National Institute of Metrology, Beijing, 100029, China
² Environment Monitoring Data Quality management department, China National Environmental Monitoring Centre, Beijing, 100012, China

*Corresponding author’s e-mail: bzh@nim.ac.cn

Abstract. Trace volatile organic compounds (VOCs) play an important role in physiochemical processes of the troposphere. Accurate measurement of ambient VOCs is needed. However, the determination of VOCs is difficult due to the large amount of water in atmosphere. A dynamic dilution and humidifying system was developed to study the impact of water on ambient VOCs measurement. Result showed that the deviation of aldehydes and ketones was much larger comparing with the BTEX compounds. And the C10-C11 compounds were more susceptible to air humidity compared with C6-C8 compounds. This showed that the hydrophilic compounds and compounds with high carbon number were more susceptible to air humidity comparing with hydrophobic compounds and compounds with lower carbon number.

1. Introduction

Trace volatile organic compounds (VOCs) play an important role in physiochemical processes of the troposphere. Photochemical reactive VOCs contribute significantly to the formation of ozone and haze precursors[1]. They also pose a serious threat to human health due to the well-known toxicity of several compounds. Therefore, precision measurement of various atmospheric VOCs is important.

The concentration value of atmospheric VOCs is usually as low as ppb or sub-ppb, which is well below the detection limit of GC-FID/MS instrument. Thus, preconcentration, enrichment, as well as other pretreatment measures are needed prior VOCs analysis. The typical pretreatment measure consists of three steps of enrichment, each of which plays a different role in pretreatment process[2]. In the first enrichment step, most of the water is removed in temperature range -50°C--10°C. In the second step, the VOCs in air is retained in a packed column in temperature range -30°C- -90°C. In the third step, the VOCs component is focused on a capillary column working in temperature range -100°C- -160°C to get a sharp chromatographic peak shape.

The humidity in ambient air poses a serious difficulty to pretreatment. The atmospheric water content is usually higher than VOCs content by dozens orders of magnitude. It is hard to remove the water without loss of the target VOCs components. Besides, even though the majority water vapor is removed in the first enrichment step, residual water content is still high considering the saturated pressure of water in -10 °C. This residual water poses a big challenge for subsequent analysis. Problems resulting from water include loss of VOCs in condensed water, blockage of cryogenic traps through the formation of ice, variability in GC retention time by overloading and damaging the
stationary phase[3-4]. The water would also lead to the calibration failure due to the deterioration of ion source. However, the impact of water vapor on VOCs measurement is largely unknown.

In this study, a humidifying system was developed to dynamically generate VOCs gas standard with ambient moisture. The impact of moisture on various VOCs measurement was investigated.

2. Materials and Methods
A dynamic dilution and humidifying system was developed by NIM (National Institute of Metrology, China) and CNEMC (China National Environmental Monitoring Centre) together. The schematic diagram of the dynamic dilution and humidifying system was shown in figure 1. The purified carrier gas was saturated by a bubbling humidifier and mix with dry carrier gas to generate humidifying carrier gas. Then the humidifying carrier gas was mixed with dry VOCs gas standard to obtain VOCs gas standard of specific concentration. The dilution ratio and humidity was controlled by mass flow controller and needle valve. The mixed gas standard containing 13 kinds of VOCs in this experiment was prepared by gravimetric method [5]. 1ppm gas standard was dilute to 2.5ppb and humidity was set to 85%R.H. (30°C) in this experiment. A preconcentration device with 3-stage of enrichment and Agilent 7890 GC with FID and MS system was used for VOCs measurement.

![Figure 1 The dynamic dilution and humidifying system](image)

3. The impact of moisture on VOCs measurement
The dry gas standard was used to calibrate the GC-MS and then the dry gas standard was humidified and analyzed by the preconcentration GC-MS system. The difference between the reference value and the measurement value was shown in table 1. The concentration of dry gas standard was used as the reference value for the humidified gas. The result showed that the deviation of aldehydes and ketones was much larger comparing with the BTEX compounds. Besides, the C10-C11 compounds were more susceptible to air humidity compared with C6-C8 compounds. This showed that the hydrophilic compounds and compounds with high carbon number were more susceptible to air humidity comparing with hydrophobic compounds and compounds with lower carbon number.

| Compound          | the reference value ×10⁻⁹mol/mol | the measured value ×10⁻⁹mol/mol | the relative standard deviation of measurement % | the deviation of measurement % |
|-------------------|----------------------------------|---------------------------------|-----------------------------------------------|-------------------------------|
| acetaldehyde      | 2.8                              | 2.5                             | 11.3%                                         | -10.2%                        |
| propaldehyde      | 2.3                              | 2.5                             | 1.5%                                          | 5.4%                          |
| isopropanol       | 2.6                              | 2.3                             | 11.1%                                         | -11.7%                        |
| ethyl acetate     | 2.9                              | 2.8                             | 5.5%                                          | -5.6%                         |
| acetaldehyde      | 2.4                              | 2.5                             | 2.3%                                          | 4.8%                          |
| acetone           | 2.9                              | 3.0                             | 1.2%                                          | 3.6%                          |
| 1,2,4-trichlorobenzene | 2.8                          | 2.6                             | 2.9%                                          | -8.2%                         |
| o-dichlorobenzene | 2.6                              | 2.5                             | 2.4%                                          | -3.0%                         |
| styrene           | 2.5                              | 2.5                             | 1.2%                                          | -0.1%                         |
4. Conclusion
A dynamic dilution and humidifying system was developed to study the impact of water on ambient VOCs measurement. The result showed that the deviation of aldehydes and ketones was much larger comparing with the BTEX compounds. The hydrophilic compounds and compounds with high carbon number were more susceptible to air humidity comparing with hydrophobic compounds and compounds with lower carbon number.

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