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Fast screening compositions of $PM_{2.5}$ by ATR-FTIR: Comparison with results from IC and OC/EC analyzers

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ABSTRACT

Chemical speciation of fine particles or $PM_{2.5}$ collected on filters is still a costly and time-consuming task. In this study, filter-based $PM_{2.5}$ samples were collected during November–December 2013 at four sites in Guangzhou, and the major components were fast screened (~7 min per filter sample) by Attenuated Total Reflectance (ATR)-Fourier Transform Infrared Spectroscopic (FTIR) in comparison with that measured by Organic carbon/Element carbon (OC/EC) analyzer and Ion Chromatography (IC). The concentrations of nitrate, ammonium, sulfate, primary organic carbon (POC) and secondary organic carbon (SOC) measured by OC/EC and IC analyzers were better correlated with their infrared absorption peak heights at 1320/cm for nitrate, 1435, 3045 and 3215/cm for ammonium, 615/cm for sulfate, 690, 760 and 890/cm for POC and 1640 and 1660/cm for SOC respectively, during polluted days ($PM_{2.5}$ > 75 μg/m^3) than during clean days ($PM_{2.5}$ ≤ 75 μg/m^3). With the evolution of a haze episode during our field campaign, the concentrations of the major $PM_{2.5}$ components displayed consistent variations with their infrared absorption peak heights, suggesting ATR-FTIR could be a fast and useful technique to characterize filter-based $PM_{2.5}$ compositions particularly during pollution events although cautions should be taken when $PM_{2.5}$ levels are low. Notably, elevated $PM_{2.5}$ mass concentrations occurred with enhanced ratios of $[NO_3^-]/[SO_4^{2-}]$ and $[NH_4^+]/[SO_4^{2-}]$, implying that nitrogenous components play vital roles in the $PM_{2.5}$ pollution events in the study region.

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Introduction

Aerosols in the atmosphere can directly and indirectly impact weather and climate by scattering and absorbing solar radiation (Wang et al., 2012; Bi et al., 2014; Guo et al., 2016; Gryspeerdt et al., 2017; Zhang et al., 2017), and thus playing an important role in global climate changes. Atmospheric aerosols, particularly fine particles or $PM_{2.5}$, have great influence on people's daily life with great economic losses and threats to human health. Air pollution due to $PM_{2.5}$ not only results in visibility degradation as observed in China in recent decades (Che et al., 2007; Chen and Wang, 2015), but also has proved to be closely related to a wide spectrum of human health risks (Brook et al., 2013; Evans et al., 2013; Silva et al., 2013; Kulmala, 2015; Bonyadi et al., 2016; Liu et al., 2016). In addition, haze particles may impose a negative effect on agricultural productivity (Chameides et al., 1999) and sulfate and nitrate aerosols can increase soil acidity through acid deposition, which cause adverse effects on the ecosystems (Kravitz et al., 2009; Cao et al., 2013).

Severe air pollution has attracted great scientific interest over the decades. An increasing number of tools and methods are now available to monitor $PM_{2.5}$ in the atmosphere (Aiken et al., 2009; Fu et al., 2014; Wang et al., 2014; Zhang et al., 2015). The chemical composition of $PM_{2.5}$ has been widely analyzed for two main parts: inorganic components and organic matters (OM). The former, which primarily consists of sulfate, ammonium, nitrate and metals, could be specifically measured by ion chromatography (Fu et al., 2014; Tao et al., 2014; Fu et al., 2015) and inductively coupled plasma–mass spectrometry (ICP-MS) (Huang et al., 2014; Tao et al., 2014a). However, OM is more complex than its inorganic counterparts because it contains a large number of compounds, which are emitted from biogenic and anthropogenic sources and can be created or transformed in the atmosphere. OM in aerosol is typically analyzed by thermal–optical methods (TOMs) (He et al., 2014; Zhang et al., 2015) or gas chromatography–mass spectroscopy (GC–MS) (Gao et al., 2013; Zhao et al., 2015; Yu et al., 2016). The former can measure total organic carbon (OC) and element carbon (EC), and thus OM (calculated by OC multiply a factor). The latter can give qualitative and quantitative measurement of individual organic compounds in aerosols. However, TOMs failed to distinguish organic components and GC–MS can only identify 10%–50% organic mass in aerosols (Coury and Dillner, 2008) and requires complex derivatization procedures to quantify polar compounds (Ding et al., 2008), which inevitably leads to artifacts during the pretreatment.

To bridge the gap between total OC measurements and molecular-level organic compound measurements, Fourier transform infrared spectroscopic (FTIR) technique has been used to identify aerosol compositions and even quantify the mass of organic and inorganic compounds in aerosols (Allen et al., 1994; Blando et al., 2001; Carlton et al., 1999; Maria and Russell, 2005; Tiwary et al., 2008; Bruns et al., 2010). FTIR is a non-destructive analytical method that provides functional group and bond information for a given sample (Reff et al., 2005). FTIR technique also has the advantages of low cost and quick analysis. In addition, IR technique has the ability to detect compounds in small quantities without extraction or derivatization to eliminate losses during chemical pretreatment (Coury and Dillner, 2009). The information provided by IR is helpful for developing an understanding of the origins, properties and behavior of the complex organic and inorganic fraction of PM. FTIR spectroscopy has been used to identify particle-phase organics formed through atmospheric chemical reactions (Day et al., 2010), to obtain insights into the origin and polarity of organics in atmospheric particles (Blando et al., 1998; Maria et al., 2002; Polidori et al., 2008), to compare the composition differences between $PM_{2.5}$ and $PM_{2.5-10}$ (Shaka' and Saliba, 2004), and to identify a Saharan dust transport to urban atmosphere (Anıl et al., 2014). Furthermore, OM and OC mass in aerosols can also be quantified using this technique so that the factor of OM/OC can be determined (Russell, 2003; Ruthenburg et al., 2014).

FTIR coupled with attenuated total reflectance (ATR) is a new technique developed recently (Anıl et al., 2014). Compared with the transmission mode of FTIR, ATR-FTIR shows some advantages such as ATR accessory can minimize light scattering by particles and allow the entire IR beam line to be purged by utilizing a sample pressure tower. Here, we collected filter-based $PM_{2.5}$ samples at different urban and rural sites in Guangzhou city in south China during dry seasons, and used the fast analysis method of ATR-FTIR to characterize the changes in aerosol compositions in comparison with chemical composition measured by OC/EC and IC analyzers. The aim of this study is to test if ATR-FTIR could be a fast and reliable method for screening chemical composition of particulate matters, especially during haze episodes.

1. Methodology

1.1. Sampling

Guangzhou, the capital city of Guangdong province with the population around 13 million, is a central city in the Pearl River Delta (PRD) region in south China. The PRD, considered as one of the largest megacities in the world, covers an area of 5.6×10^4 km^2 with a population of ~43 million and has experienced rapid industrialization and environmental changes in the last several decades. Four sites in Guangzhou were carefully chosen to collect $PM_{2.5}$ samples including two urban sites (SZ and YJ) and two rural sites (JL and WQS). The detailed descriptions and geographic locations about the sampling sites can be found elsewhere (Yu et al., 2016). Briefly, SZ (23.13°N, 113.27°E) and YJ (23.13°N, 113.32°E) are located in the center of the city, with heavy traffic and diverse commercial activities. JL (23.30°N, 113.57°E), surrounded by forests, is in the northeast of Guangzhou, about 46.8 km from the city center. WQS (22.71°N, 113.55°E) is a small town located at the center of the PRD, approximately 55 km southeast of the city center and is mainly affected by transported pollutants from the PRD regions.

A total of 192 daily $PM_{2.5}$ samples (96 quartz + 96 Teflon) were simultaneously collected on pre-weighted quartz fiber (prebaked for 6 hr at 450 °C, 8 × 10 inches, Whatman, Maidstone, UK) and Teflon filters (47-mm diameter, Whatman,

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