APPLICATION NOTE

FT-IR Microscopy

Authors:

Mitsuhiko Morimoto

PerkinElmer, Inc.
Japan

Osamu Nagafuchi

Shiga Prefecture University

Augmenting Standard Methods of Measuring Airborne $PM_{2.5}$ Using IR Imaging

Background

Global concern is growing over the amount of pollution in the atmosphere and the effect on human health. A major source of pollution is particulate matter (PM), solid or liquid particles suspended in the atmosphere. The International Agency for Research on Cancer (IARC), and World Health Organization (WHO), designate particulates as Group 1 carcinogen. They have the potential for causing health problems in humans due to inhalation of the particles. The smaller the particles, the further they can get into the respiratory system. There are various classifications of the PM defined by the particle sizes, such as PM_{10} (particles less than 10 micrometers in size) and $PM_{2.5}$ (particles less than 2.5 micrometers in size). $PM_{2.5}$ is of particular concern and has been the subject of many health studies linking to respiratory diseases and increased occurrences of lung cancer.

The major sources of $PM_{2.5}$ are industrial combustion, road transport (from diesel emissions), burning of fossil fuels and small-scale waste burning. There are also natural sources, such as volcanoes and sea spray.

PerkinElmer
For the Better

Due to the health effects of PM, governments across the globe have created regulations and set limits for the ambient concentration of particulates. These limits for a selection of territories are shown in Table 1.

Table 1. Concentration limits for PM

		PM10	PM2.5
China	Yearly average	70 μg/m³	35 μg/m³
European Union	Yearly average	40 μg/m³	25 μg/m³
Japan	Yearly average	N/A	15 μg/m³
South Korea	Yearly average	50 μg/m³	25 μg/m³
United States	Yearly average	N/A	15 μg/m³

N/A - daily limits set instead of yearly averages

Airborne PM has the ability to be carried hundreds of miles from its source and hence, can often cross territorial boundaries.

Cross-border Study of PM using imaging FT-IR

This application note will demonstrate the utility and useful information that can be obtained by the use of imaging FT-IR microscopy. A study has been performed using data collected in South Korea, China and Japan.

The reference method for measuring $PM_{2.5}$ is a manual gravimetric method. Samples of PM are taken by pumping ambient air through a size-selective inlet, followed by a filter. The concentration of PM is determined by measuring the change in mass of the filter before and after the sampling, and combining the result with the volume of air sampled. Figure 1a shows an example of the air sampling equipment, consisting of a cascade impactor and suction pump. Figure 1b shows an exploded diagram of the cascade impactor.

Figure 1a. Suction pump and cascade impactor

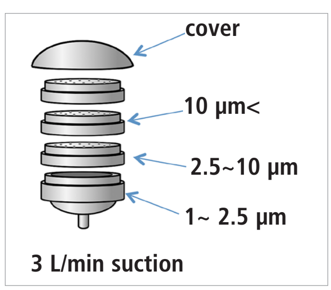

Figure 1b. Cascade impactor

The filter substrate used in this experiment was made from polycarbonate, a material that is suitable for IR Transmission measurements. The cascade impactor was deployed at three sites; Seoul, Beijing and Tokyo, by placing it outside the window of the chosen building. Pumped sampling was carried out for half a day at a rate of 3 L/min. The arrangement used in Beijing is shown as Figure 2.

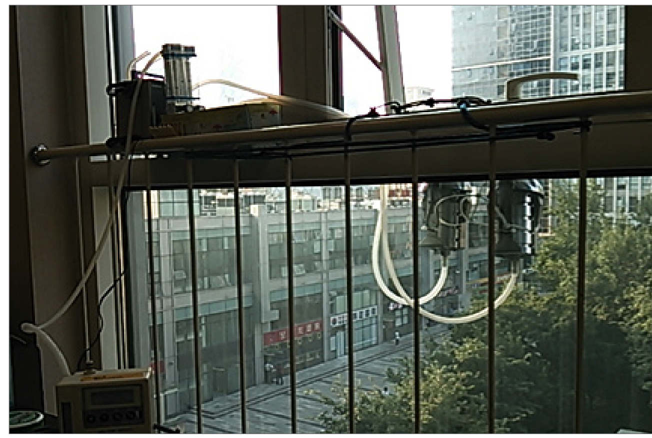

Figure 2. Air sampling in Beijing

Once the air sampling is complete the polycarbonate filter can be removed for analysis. The standard technique of gravimetric analysis is able to determine the total mass of the $PM_{2.5}$ collected during the sampling time. However, it is not possible to determine the chemical composition of the PM. Infrared spectroscopy is an established technique for both chemical identification and quantitation of the materials present. An infrared spectrum from an air sampling experiment, collecting $PM_{2.5}$, is shown in Figure 3.

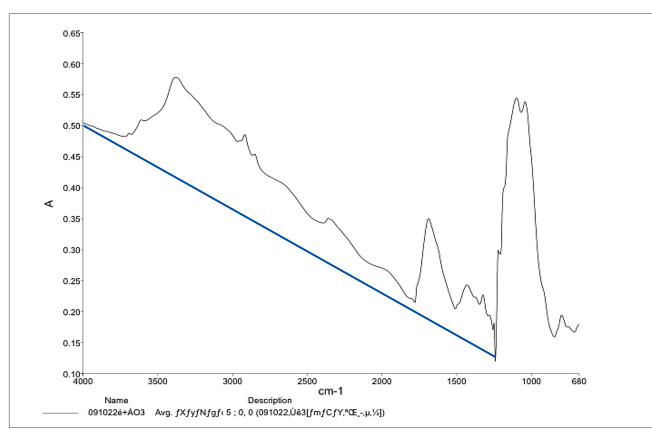

Figure 3. Infrared absorption spectrum of $PM_{2.5}$, baseline slope mainly due to black carbon

$PM_{2.5}$ consists mainly of nitrates, sulfates, black carbon and organic carbon. The infrared spectrum shows specific absorptions due to all of these materials with the exception of black carbon. The presence of black carbon particles shows up in the infrared spectrum as a baseline slope due to the scattering of the infrared beam. Spectra were collected on a PerkinElmer Frontier FT-IR spectrometer. This instrument can be equipped with a Spotlight 400 Imaging FT-IR microscope as shown in Figure 4.

Figure 4. PerkinElmer Frontier FT-IR and Spotlight 400

The Spotlight 400 allows for the collection of infrared chemical images from materials. In the analysis of $PM_{2.5}$ it is capable of determining the spatial distribution and identification of individual particles of the materials deposited on the polycarbonate filter. A camera inside the instrument collects a visible image of the sample. The infrared spectra and chemical image are then collected over the entire visible image region. Data collection takes approximately five minutes for the whole filter using data collection parameters shown in Table 2.

Table 2. Measurement conditions for $PM_{2.5}$ IR Imaging experiment

Measurement Conditions	
Measurement Method	IR-Imaging .Transmission
Resolution	16 cm^{-1}
Number of scans per pixel	1
Wavenumber Range	4000-680 cm^{-1}
Sample Size measured	1000 µm × 1000 µm
Pixel size	6.25 µm × 6.25 µm
Background	Polycarbonate film
Total number of spectra	23600
Measurement Time	About 5 min.

Images collected from the three sites are shown in Figure 5. The visible image shows the particle distribution on the filter, the IR images show the spatial distribution of different components. The IR images can be calculated as Total Absorbance in the infrared region of the spectrum, or they can be calculated for individual components of the PM by selecting appropriate wavelength regions. At each pixel point in the image (every 6.25 micrometers) there is a complete infrared spectrum available. The IR absorbance for the individual component is directly related to the concentration of that component, represented by the pixel color scale shown in each image.

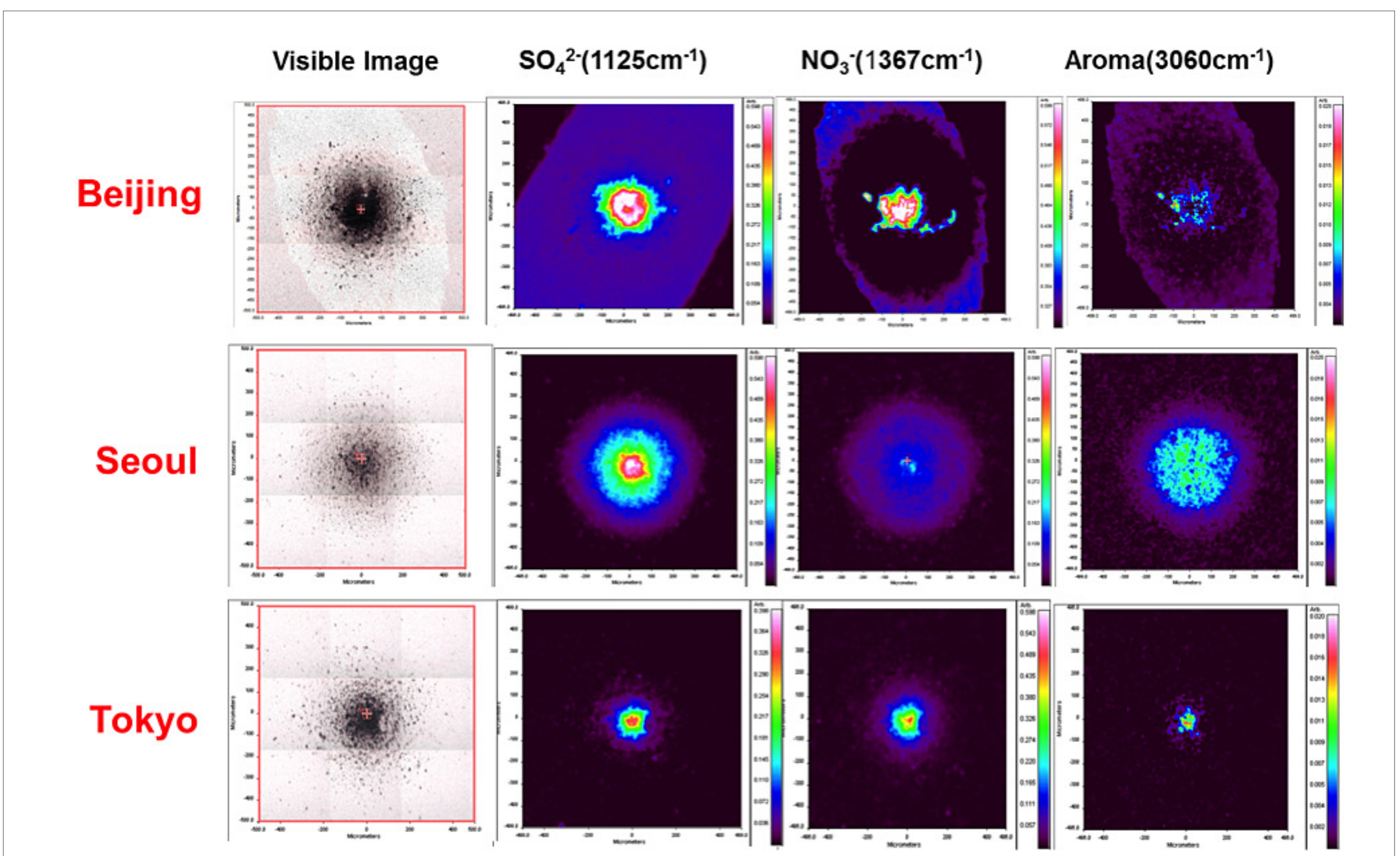

Figure 5. Visible images (left column) and IR images for the individual components present in $PM_{2.5}$

The visible images show that overall there is a larger amount of $PM_{2.5}$ collected during the experiment in Beijing compared to the other sites. If using conventional gravimetric analysis, this is the only information that would be obtained. IR imaging gives the additional information as to the chemical nature of the PM at the different sites.

Quantitative Determination of Ion Concentrations

A series of 10 experiments were performed where IR spectral data was collected and the concentrations of ions collected on the filters were determined off-line by the use of Ion Chromatography. The IR spectra and the results from the Ion Chromatography were then used in the Spectrum Quant software using a PLS1 quantitative algorithm to generate calibrations for he concentrations of the ions. The calibration plots are shown in Figure 6.

The plots show excellent correlation (0.9854 for sulphate, 0.9578 for nitrate) between the IR estimated values and the standard reference values from the Ion Chromatography measurements, indicating that IR image data could be used as an accurate estimation of the concentrations of ions collected in the $PM_{2.5}$ experiments. These calibrations were then applied to the data collected at the three sites and the results are reported in Figure 7.

This data (the ion concentrations and the organic carbon from the IR images) demonstrates that, at the time of measurements, there did not appear to be any significant cross-border pollution of $PM_{2.5}$, especially into the Tokyo area.

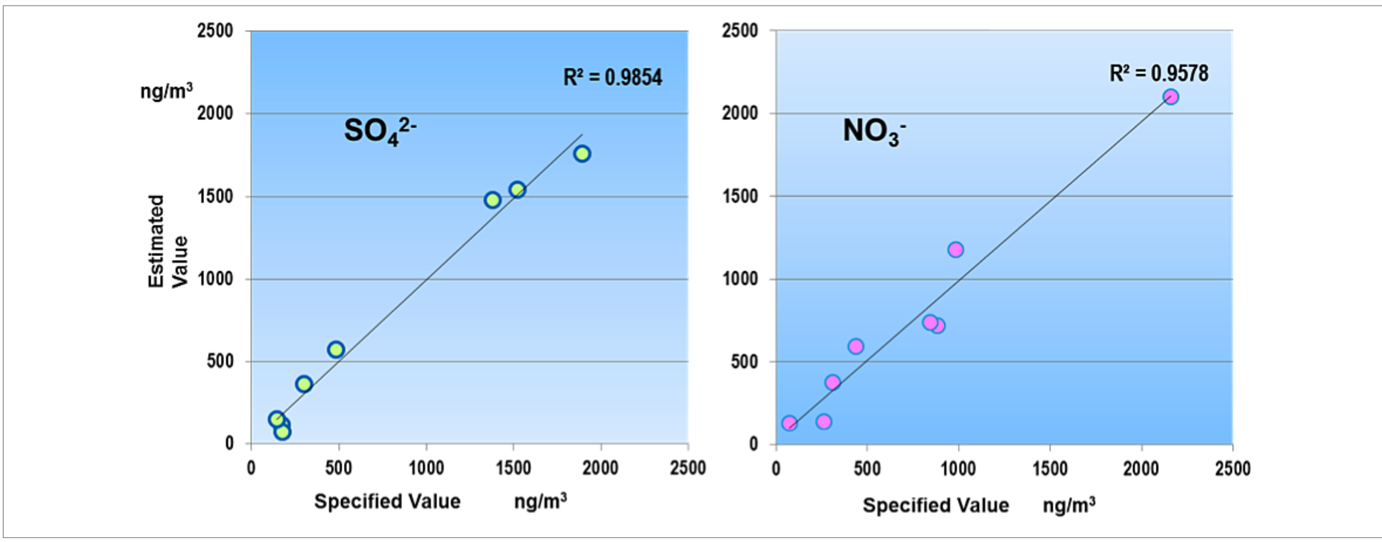

Figure 6. IR estimated values vs. Ion Chromatography reference values

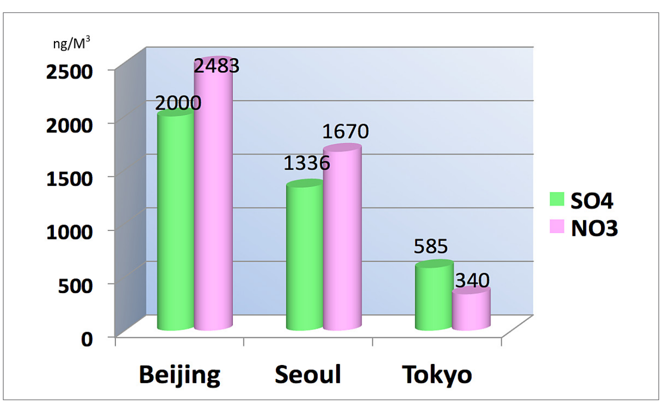

Figure 7. Quantitative measurement of ions in $PM_{2.5}$ at 3 sites

Summary

The standard gravimetric method for the measurement of $PM_{2.5}$ is used to give the total amount of $PM_{2.5}$ collected. The use of IR imaging expands the measurement possibilities by giving information about the individual types of materials present in the collected particles. The information from the IR imaging experiment is not only qualitative (i.e. identification of the particulates), but can also be calibrated to give quantitative information on the components present. The IR imaging measurement will take only five minutes, whereas Ion Chromatography requires solvent extraction of the particulates and would take around 20-25 minutes per sample.

In addition, the IR imaging results immediately show the level of the $PM_{2.5}$ pollutants in a clear and visible display.

The data presented in this application note has demonstrated that there was definitely no cross-border contamination into the Tokyo area from higher polluted territories during this study.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

PerkinElmer®

011750_01