Continuous Particulate Monitor with X-ray Fluorescence PX-375

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Particulate matter (PM) is one of the major contributors to air pollution. There is a need for simultaneous measurement of PM and its chemical properties to adjust processes parameters quickly and identify emission sources. The PX-375 simultaneously measures the mass concentration and elemental composition. The PX-375 relies on the beta ray attenuation and x-ray fluorescence techniques. A comparison with the manual analysis technique (ICP-MS) shows good correlation with field data collected.

Introduction

Particulate matter (PM) has attracted much attention as one of the key items in air pollution. In order to track where the PM is being generated and the mechanism of release, it is critical to rapidly analyze material substances and their constituents. HORIBA developed the PX-375 to continuously measure mass concentration by the beta ray attenuation and element concentration by X-ray fluorescence. By developing our own unique sample filter tape, the PX-375 is capable of measuring mass and element concentration with high-sensitivity and time resolution. A third party organization confirmed favorable correlation results between the PX-375 and the inductively coupled plasma mass spectrometry method (ICP-MS). This paper introduces the validity of field-testing using the PX-375.

PX-375 overview

HORIBA's PX-375 is capable of providing important data to locate emission sources and their potential health effects. The PX-375 is able to analyze without pre-processing collected samples, making it possible to attain the same time resolution of mass measurement compared to that of a sample measured in 1-hour intervals.

- Capable of simultaneous measurement of mass and element concentration in the field with one analyzer unit
- Utilizes beta ray attenuation for mass analysis and X-ray fluorescence for elemental analysis
- Capable of component analysis by utilizing a proprietary filter tape
- Camera allows observation of particle sample collection on the filter

Figure 1 Continuous Particulate Monitor with X-ray Fluorescence PX-375

Table 1 Specifications of PX-375

Mass analyzer	
Measuring principles	Beta-ray attenuation
Measurement range	0-200/500/1000 μg/m^3
Repeatability	Within ±2% for equivalent film value
Minimum detection limit (2σ)	Within ±4 μg/m^3
Sampling cycle	0.5/1/2/3/4/6/8/12/24 hours
Filter tape advance	20/25/50/100 mm
Element analyzer	
Measuring principles	Energy dispersive fluorescent X-ray spectroscopy
Detectable elements	Al-U
Primary X-ray filter	Auto switching at 15 kV, 50 kV
Detector	SDD (Silicon Drift Detector)
Sample image	CMOS camera
X-ray safety mechanisms	X-ray interlock system Key switch X-ray indication light
Common part	
Power supply voltage	AC100V-240V ±10% 50/60Hz ±1Hz
Power consumption	400 VA or less in normal state
External dimensions	Approx. 430 mm (W) x 560 mm (D) x 285 mm (H) (excluding projecting parts and cyclones)
Ambient operating temperature	5-35°C
Performance guarantee	10-30°C
Relative humidity	80% or less (5°C to 30°C) Linearly reduced up to 80 % to 65 % (30°C to 35°C) No condensation
Mass	Approx. 49 kg

Figure 2　Screen of measurement monitoring

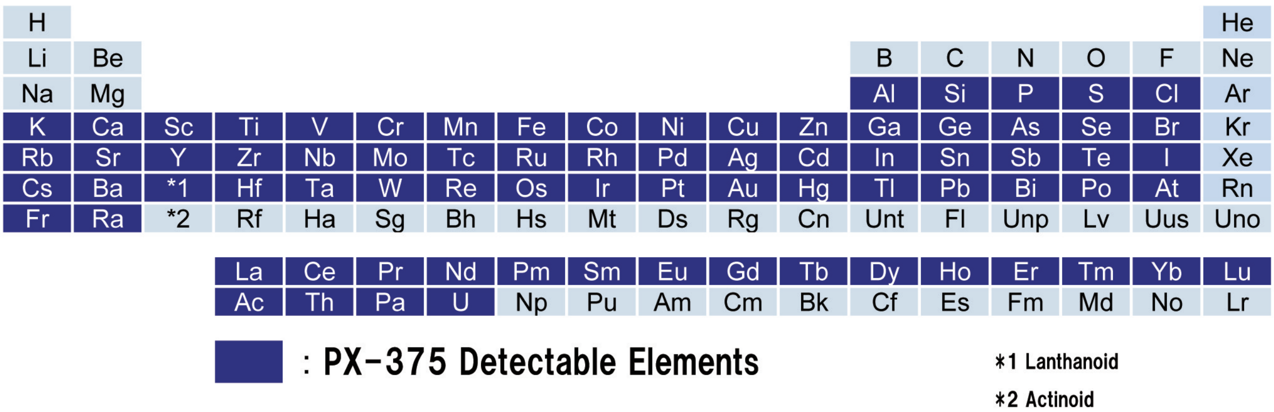

Figure 3　Detectable elements of PX-375

Figure 1 shows the appearance of the PX-375 unit, **Table 1** lists the specifications and **Figure 2** displays the measurement screen and user interface.

Detectable elements

The PX-375 is capable of detecting elements from Aluminum to Uranium (with respect to the Periodic Table of Elements in **Figure 3**) for elemental analysis. For determining quantity, The PX-375 requires a standard reference material. Using National Institute of Standards and Technology (NIST) SRM2783[1], the PX-375 calibrates and determines the quantity of 15 elements (Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Pb). It is also possible to quantify other elements provided a standard reference material.

Filter tape for sampling

Most PM analyzers utilize filter tape composed primarily of fiberglass or PTFE. Fiberglass has a relatively strong tensile strength, but has many impurities that interfere with the

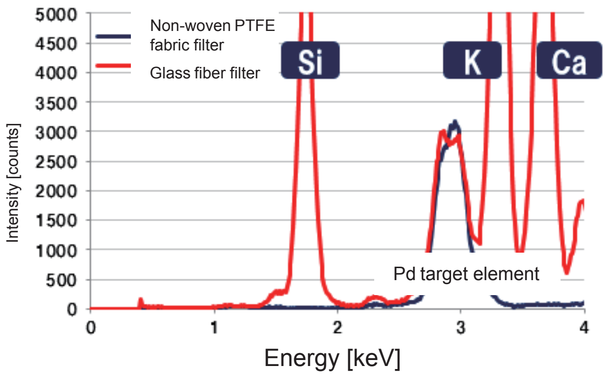

Figure 4　Comparison between X-ray fluorescence spectra of glass fiber filter and newly developed filter

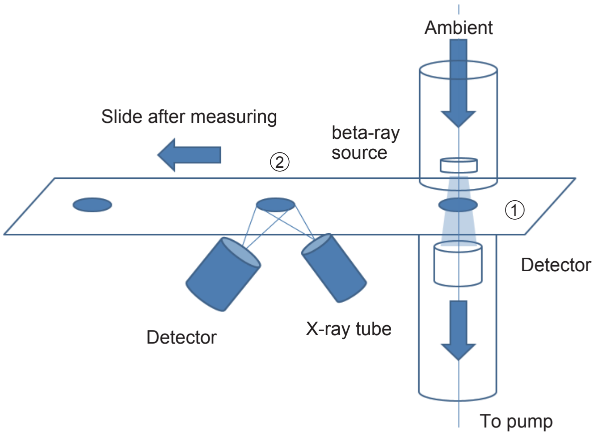

Figure 5 Measurement flow
Sampling and mass measurement at position (1) elemental measurement at position (2)

measurement. In addition, the signal-to-noise ratio of X-ray fluorescence signal declines with increasing scattered X-ray strength (background) due to its high density. PTFE is relatively weak tensile strength and its filter has the characteristic of uneven bending due to variation of suction resistance by the quantity of the collected particles. These factors contribute significantly to error during X-ray Fluorescence analysis. The PX-375 utilizes HORIBA proprietary filter tape containing few impurities, while having the physical strength of fiberglass and the water repellency of PTFE. **Figure 4** conveys the spectrum of X-ray fluorescence of a fiberglass filter and the developed filter tape.

Measurement flow

Figure 5 conveys the flow of the measurement: ① measures the mass concentration of particles caught in the filter tape which have been graded using a size grading device (TSP [Total Suspended Particulate]: PM10, PM2.5, PM1). Calculates the mean of the measured mass concentration during the sampling period. ② Next, the filter tape conveyor translates the sample for a fixed distance within the analyzer and performs X-ray analysis

Figure 7 Measurement point of field test
(Map data ©2018 GeoBasis-DE/BKG (©2009) Google, Inst. Geogr. Nacional)

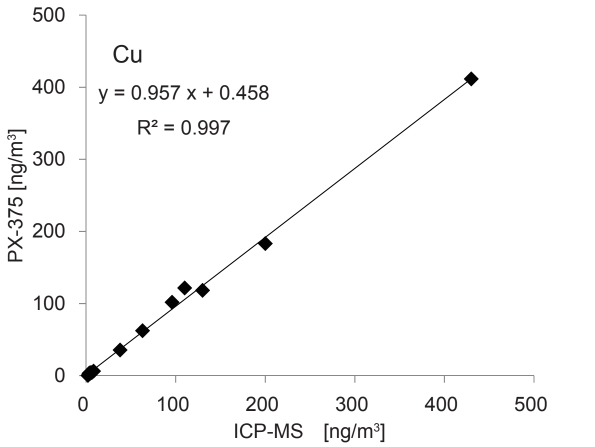

Figure 6 Correlation between Cu concentration results by PX-375 and ICP-MS

Table 2 Correlation factor for detectable elements

Element	Al	Ca	Cr	Fe	Ni	Zn
Correlation factor	0.92	0.88	0.88	0.96	0.86	0.94
Element	Pb	S	K	Cu	Mn	
Correlation factor	0.91	0.99	0.99	0.99	0.96	

at 15 kV and 50 kV, calculating element concentration of the sample. If sampling time is one hour (for example 14:00 to 15:00), the filter tape moves at 15:00 and element analysis starts at 15:05. The standard analysis time is 1000 seconds (500 seconds for each 15 kV and 50 kV) which leads to mass concentration and element concentration results ready by 15:20. Filter tape intervals can be set to 20/25/50/100 mm and therefore the time until the results of both measurements may vary by settings.

Verification

To confirm the effectiveness the X-ray fluorescence analysis utilized by the PX-375, results were compared with a conventional wet decomposition ICP-MS. Samples used for this comparison were collected for 1 hour and analyzed on the PX-375 before destructively analysis on the ICP-MS. The analysis was carried out in accordance to the inorganic element test methodology[2] of fine particulate matter (PM2.5) component manual in the atmosphere.

As an example, **Figure 6** conveys the comparison result of copper (Cu), and **Table 2** lists the linear regression coefficient of each element. Albeit the coefficient of correlation varied according to element, a strong correlation was observed.

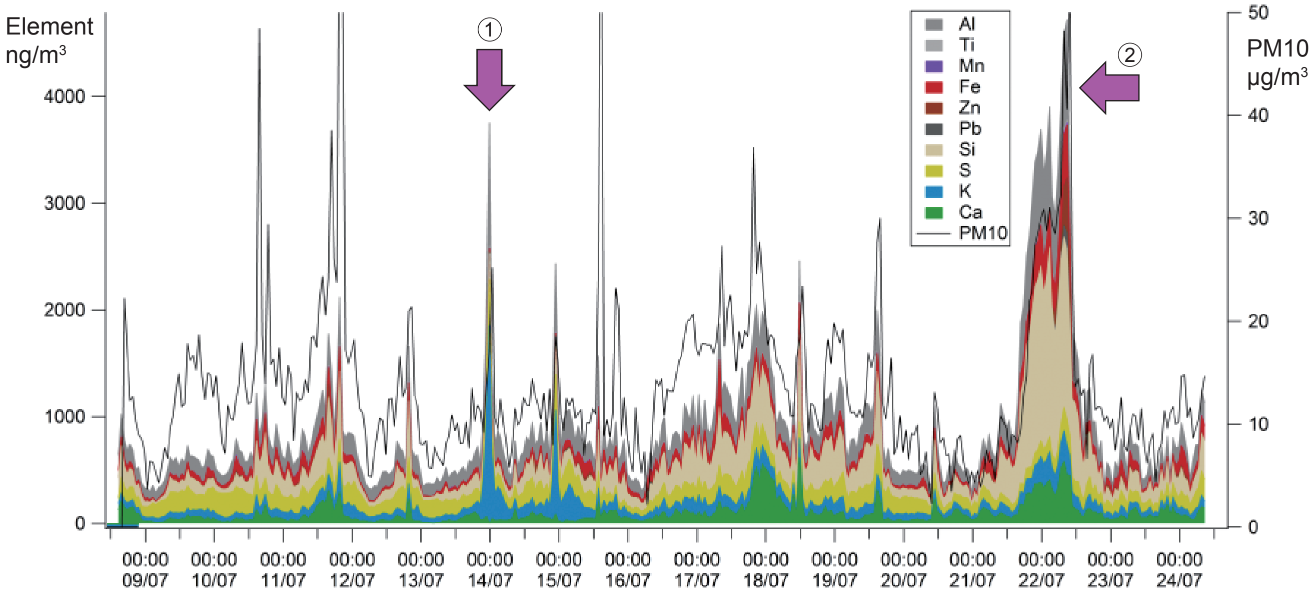

Figure 8　Elemental concentrations of PM10 obtained with PX-375 (Air data Lorraine)[3]

Example of Implementation and Field Testing

Example of field testing in France[3]

The field test took place from July 9th to July 24th 2015 with a one hours sampling interval. **Figure 7** shows the location of the device and **Figure 8** displays the measurement results. After confirming activity around the location of the device, two points in **Figure 8** accurately convey the effects two local events: ① a local firework event, and ② a fire at a recycling factory 20 km away. The PX-375 was able to monitor the effects of the event on the ambient atmosphere.

Implementation example at the ministry of the environment control monitoring station (Japan)

The PX-375 was installed in four locations for continuous hourly measurement of PM2.5 components, starting April of 2017.

Figure 9 displays the monitoring location - (巻) Maki: National acid deposition monitoring station on Niigata Maki, (東京) Tokyo: Tokyo Metropolitan Res. Inst. for Environmental Protection, (五島) Goto: National acid deposition monitoring station, (福岡) Fukuoka: Fukuoka University[4]. Implementing the PX-375 at these locations allowed the Ministry to monitor the details of domestic outbreak sources as well as transcontinental pollution. This implementation contribute to PM2.5 countermeasures. The measurement results at each monitoring station are published on measurement results at each monitoring station are published on the Ministry of the Environment's website[5]. **Figure 10** displays an example of the measurement results.

Analysis example of "yellow sand"

The PX-375 measurement results confirmed the occur-rences of "yellow sand days" as announced by the Meteorological Agency from May 6 to May 8, 2017[6]. "Yellow sand" is a meteorological phenomenon in which strong winds carry fine dry soil particles from the deserts in Mongolia, northern China, and Kazakhstan. The clouds of soil particles or "yellow sand" contain industrial pollutants that are carried through the atmosphere to neighboring countries. Concentration traces of ingredients in yellow sand, such as Al and Ca[2] and abnormal events such as yellow sand occur injust several hours. This implementation example demonstrates the effectiveness of applying the PX-375's high time resolution. The PX-375 capture the specific events from these field examinations and demon-strates the effectiveness of the consecutive measurement.

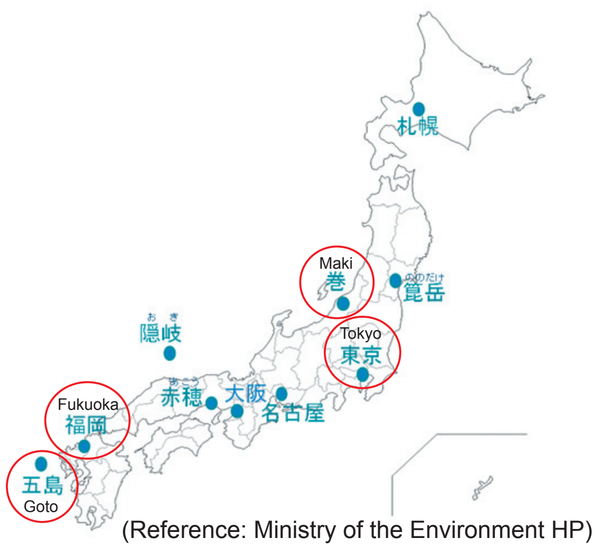

Figure 9　Monitoring stations of PX-375 shown by Red circles

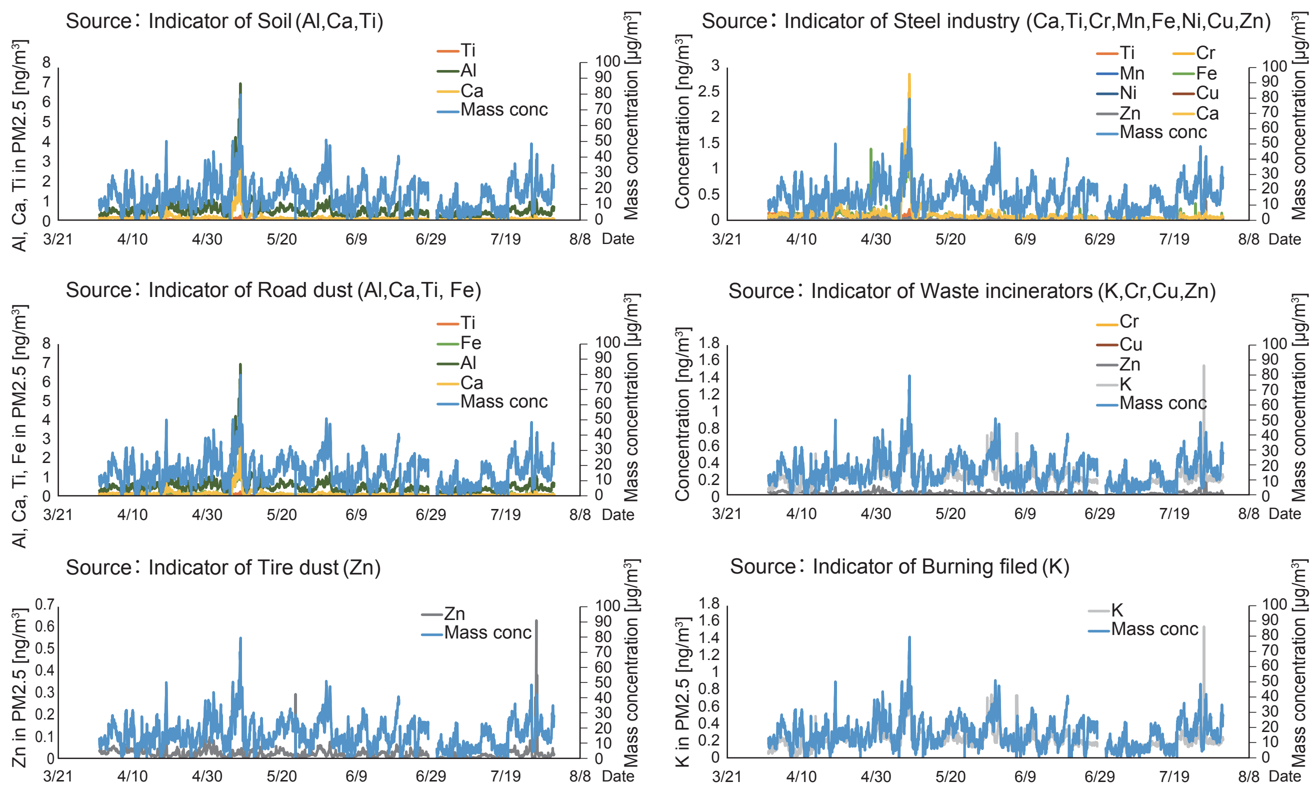

Figure 10 Measurement example obtained with PX-375 at Ministry of Environment Observatories

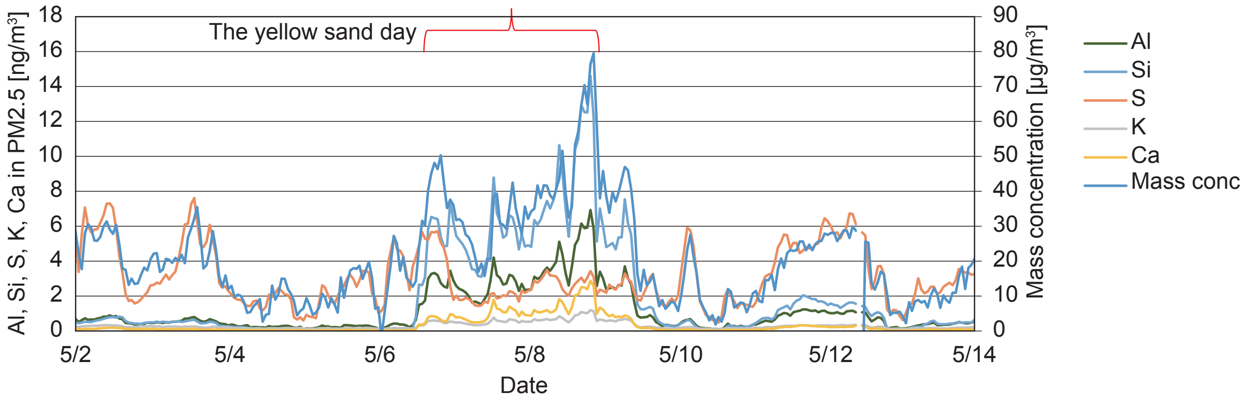

Figure 11 Influence of Yellow sand on measurement results of PX-375

Future Prospects

The PX-375, as a single instrument, has proven its effectiveness in its capability to measure PM2.5 mass and element concentration. Conventional analysis techniques are unable to capture rapid outbreaks of unique element concentrations during given periods due to cost and time. The PX-375 provides continuous data measurement at the high time resolution onsite and users are capable of understanding outbreaks by studying relative increase and decreases of element concentration.

This capability enables users to assess trends and to investigate unique values by performing a more detailed analysis. Long-term measurement will aid in the knowledge of changes in the outbreak source and the characteristics at a regional level, while the concentrations of inorganic elements that PX-375 measures contributes very little to ambient pollution, they can be used as key indicators for investigating the outbreak sources. Measuring other pollutants such as sulfur dioxide and nitrogen oxides for one hour, the PX-375 can contribute to analyzing outbreak sources by modeling with the Chemical Mass Balance method and the Positive Matrix Factorization method. The PX-375 enables users to analyze highly concentrated events and discern whether they are longterm or short-term events. In addition, what kind of elements are being released into the atmosphere and if the pollution migrated from foreign countries. It gives users the capability to understand pollution sources and means to take effective countermeasures.

Conclusion

Widespread air pollution, such as PM2.5, is considered a shared problem in Asian countries because no borders bind it. Not limited to mass concentration measurement, a more detailed analysis of pollution needs to done in order to take more effective countermeasures against PM2.5.

HORIBA develops measurement and analysis equipment for automobile, environmental, science, semiconductor, medical and various fields. We provide the opportunity to create solutions to problems by developing analysis and measurement techniques. In doing so, we continue to be engaged as an active member in the maintenance of the global environment and industrial development.

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