PM2.5 Measuring Technique and Future Development in Air Quality

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Recently, the Asian countries face environmental pollution with economic growth. Especially air pollution such as PM2.5 is recognized as transnational common issues and Asian countries are dealing with the air pollution problem through intergovernmental cooperation. We describe the features of APDA-375A and the possibility of combined Analyzer as key to the PM2.5 air pollution.

Introduction

While the concentration of major air pollutants such as Carbon Monoxide (CO) and Sulfur Dioxide (SO_2) in the air has decreased, the concentration of photochemical oxidants is on a slight increasing trend. Also, with regard to the fine Particulate Matter (called "PM2.5" below) described in the 2009 environmental standards, an environmental monitoring network is being prepared. However, in FY2012, 43.3% of the environmental standard was achieved at air pollution monitoring stations, and 33.3% of the standard was achieved at motor vehicle exhaust monitoring stations, and effective counter-measures are being required. Atmospheric environmental problems are one of the major issues in building a recycling-oriented society that can continuously grow and must be solved on a global scale, not just in Japan. Measuring the air is different from measuring gases emitted from fixed sources such as garbage incineration or power generation--the concentration of the substance to be measured that diffuses into the air is generally low. For that reason, high-sensitivity, stable measurements are required for measuring components in the air. This paper will introduce the features of the newly developed fine particulate matter concentration monitoring device (APDA-375A) for monitoring air pollution based on the HORIBA Group's measurement technology that has been cultivated over long years, and will also introduce the HORIBA Group's applications for measurement technology.

What Particles are in the Air?

There are various particles in the air. In Japan, these are defined by the Air Pollution Control Law and environmental standards, etc., and Table 1 shows a list of these. In Japan, as an environmental standard, the term Suspended Particulate Matter (called "SPM" below) was set in 1973 to mean suspended particles in the air whose diameter is 10 μm or less. Some particles have natural origins, such as salt water particles from the sea or soil particles such as the yellow sand that flies up in the wind.

Table 1 Particles in the air

	Descriptions
Soot and Dust	Substances (such as soot) that are generated when burning fuel or other substances, or when electricity is used as a heat source. In the Air Pollution Control Law, this is specified as one type of 'soot and smoke'.
Dust	Generated by things such as crushing objects and sedimentation, or substances that disperse through the air.
Particulate Matter	In the Air Pollution Control Law, this substance is specified as an item found in automotive exhaust gas.
Secondary Particulate	Particulate matter made by gaseous substances being pulverized by sunlight, etc. in photochemical reactions in the air.
Dust fall	Refers to particulates such as dust and soot that fall to the earth due to things such as gravity and rain.
Suspended Particulate Matter	Particulate matter suspended in the air, what remains after particles with particle diameters larger than 10 μm have been removed
Fine Particulate Matter	Particulate matter suspended in the air, what remains after particles with larger particle diameters have been removed using a sizing device that can separate 50% of the particles with particle diameters of 2.5 μm.

Table 2 Environmental criteria

Environmental criteria	Value for one hour	Average value for one day	Average value for one year
SPM	0.20 mg/m^3	0.10 mg/m^3	–
PM2.5	–	35 μg/m^3	15 μg/m^3

Other particles have man-made origins, and some examples of these are the soot that is discharged from factories and automobiles. For automobiles, countermeasures such as improving and developing combustion and injection systems exist, such as developing Diesel Particulate Filters (DPF). For factories, there are various countermeasures, such as optimizing combustion temperatures and installing electrostatic precipitators. In FY2012, due to these measures, both air pollution monitoring stations and motor vehicle exhaust monitoring stations achieved 99.7% of the environmental standards. On the other hand, because PM2.5 with a particle diameter of 2.5 μm or less gets into the deep part of the lungs and affects the cardiovascular system and respiratory system, this was included in the environmental standard in 2009 and is being continuously monitored, the same as SPM. Table 2 below shows the environmental standard values for particulate substances.

The Need to Continuously measure PM2.5

The environmental standards for the PM2.5 measurement require that the daily average value, which is the n-th (equivalent to 98%) value from the lowest value of the daily average values over a year (effective measurement date[*1]), be 35 μg/m^3 or less and that the annual average value be 15 μg/m^3 or less. The measurement methods for this are 1) Mass concentration measurement methods using dust filtration and 2) Automatic measuring machines recognized as being able to get values equivalent to the mass concentration measured using the dust filtration method. However, to do the long-term evaluations according to the environmental standards, the annual measurement time needs to be at least 6,000 hours, and if this is converted into a number of days, it would be an effective number of measurement days equivalent to at least 250 days. The dust filtration method (standard measurement method) given in 1) Uses a device that meets the conditions listed in the PM2.5 measurement sampler for air (JIS Z 8851). The principle of this is to draw in particulate substances from the air at a constant flow rate, and use a sizing device to collect only the particles with particle diameters of 2.5 μm or less in a filter. The collected filter is then humidified in temperature-controlled and humidity-controlled (21.5±1.5°C, 35±5%) conditions, then the mass before and after collection is found using a scale, and the mass concentration is calculated based on the mass of the samples drawn in during the collection period. In a 2009 report by the Specialist Subcommittee on Measuring Fine Particulate Matter under the Atmospheric Environment Subcommittee of the Central Environment Council, the collection time for continuous monitoring is from 12 am to 12 midnight, but when tests and research are done to evaluate the equivalence with automatic measuring machines, this is not the limitation. In that case, the evaluation tests to test equivalence with automatic measuring machines implemented by the Ministry of the Environment evaluate average values from 12 noon to 11 am the following day. In this way, if we consider the time it takes to take measurements, for practical reasons, when measuring PM2.5, it becomes essential to use an automatic measuring machine to take continuous measurements.

*1: Effective number of measurement days: Number of days when the measurement time during one day was at least 20 hours

Basic Conditions an Automatic Measuring Machine should meet

The automatic measuring machines described above must be equivalent to the measurement results from the dust filtration method. The following are the main conditions that are required for automatic measuring machines.

1) A good linear relationship must exist between the standard measurement method (dust filtration method) and the parallel measurement test, and the differences in the two measurement values must be within a certain range.
2) As a feature of the sizing device, the 50% cut-off diameter must be 2.5 μm. As prescribed in JIS Z 8851, the performance must meet these requirements: the particle diameter of 50% must be 2.5±0.2 μm, and the slope prescribed by the ratio of the particle diameter of 20% to the particle diameter of 80% must be 1.5 or less. If there is no sizing device, the same performance must be met.
3) As a daily average value, it must be possible to measure a measurement concentration range of 2-200 μg/m^3.
4) The distance from the sizing device to the particle collection area must be 1.5 m or less, and the height of the air sample inlet must be within 3-10 m from the ground surface.
5) It is desirable for the unit to have a function that controls changes in mass concentration due to changes in relative humidity.

In particular, with regard to the effects on mass concentration with respect to relative humidity, the major components that make up PM2.5 are particulate substances called secondary particles which were particulated by gaseous substances in photochemical reactions, and this includes many deliquescent particles such as ammonium sulfate and ammonium nitrate. With the dust filtration method, it is difficult for these particles to have effects because the filter is humidified, but with an automatic measuring machine, the filter is not humidified. In addition, because the mass concentration is lower than with SPM, the deliquescent secondary particles have a larger effect, and under very humid conditions such as in the summer, the effects of changes in relative humidity are pronounced. For that reason, a dehumidifier is required to reduce the effects of relative humidity.

Development of a Device for Measuring the Concentration of Fine Particulate Matter

PM2.5 has many factors that can cause errors, such as being affected by humidity, so the Ministry of the Environment did equivalence evaluation tests[*2] in Niigata (non-urban area) and Kawasaki (urban area) in the summer and winter. In the first equivalence evaluation test, APDA-375A (Figure 1) was evaluated by the Ministry of the Environment as having equivalence, and is currently being used by local government as a continuous monitoring device for the air environment. For details on the equivalence evaluation results, please go to the Ministry of the Environment's webpage entitled "Fine Particulate Matter (PM2.5) automatic measuring machine equivalence evaluations" *[In Japanese]*. We would like to introduce the features of APDA-375A.

Figure 1 APDA-375A

*2: Equivalence evaluation test: Outdoor test measuring principle that evaluates whether the automatic measuring machine is equivalent to the mass concentration measurement method that uses dust filtration.

Measurement principle

The SPM in the air is introduced from the air sample inlet, then the sizing device sorts the particles into only the particles with a particle diameter of 2.5 μm or less and collects them in a collection filter. When that filter is irradiated with a type of beta-ray (β-ray) radiation, the β rays are absorbed proportionally to the collected particle mass. (Figure 2) The mass is calculated from the absorbed amount, and the mass concentration is found based on the drawn-in air volume. When taking precise, low-concentration measurements with the β-ray absorption method, in principle, problems exist such as establishment errors due to β-ray decay, variations in the β-ray permeation amount due to the thickness and material properties of the filter and other variations, and the effects of moisture due to changes in relative humidity. There are various methods for solving these problems, such as 1) Increasing the strength of the β-rays, 2) Increasing the β-ray permeation amount by making the collection filter thinner to reduce the amount absorbed by the filter itself, and 3) Using a dehumidifier or other such device to minimize the effects of moisture. In the case of 1), if the radiation is 10 MBq or less, it does not fall under the category of the radioisotopes prescribed in the Act Concerning Prevention of Radiation Hazards due to Radioisotopes, Etc., and the strength can be increased. However, if we consider safety and other considerations, it is definitely better for the radiation source to have a low strength. In the case of 2), although the distance can be shortened, adhering to the same structure as the SPM concentration measuring device (APDA-370) means that

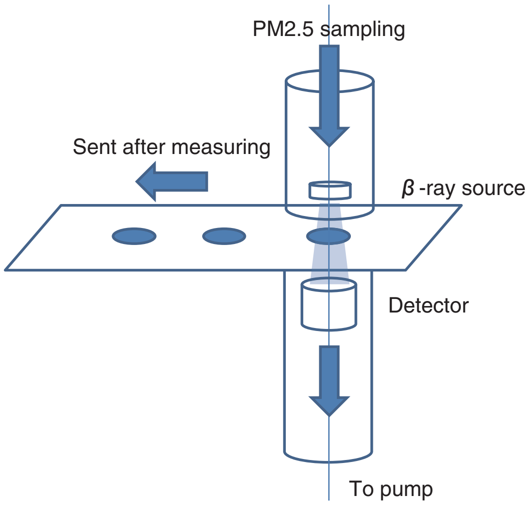


Figure 2 Measurement principles

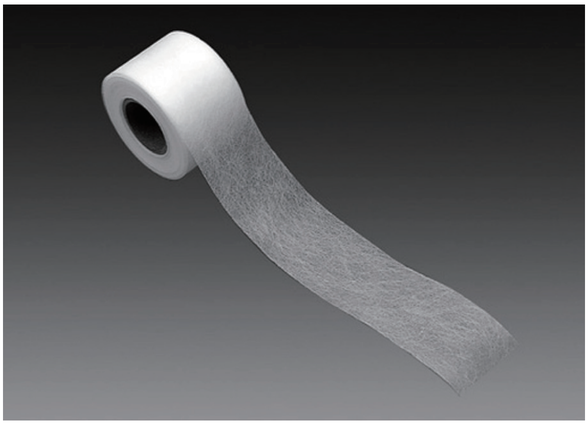
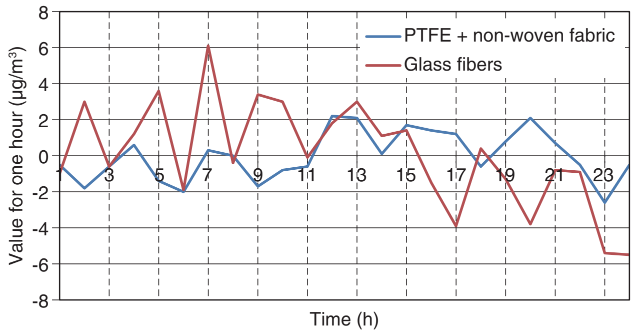


Figure 3 TFH filter



Filter material	Standard deviation (σ)
PTFE + non-woven fabric	1.4 $\mu g/m^3$
Glass fibers	2.9 $\mu g/m^3$

Figure 4 Reading values for air that doesn't contain particulates (blank test)

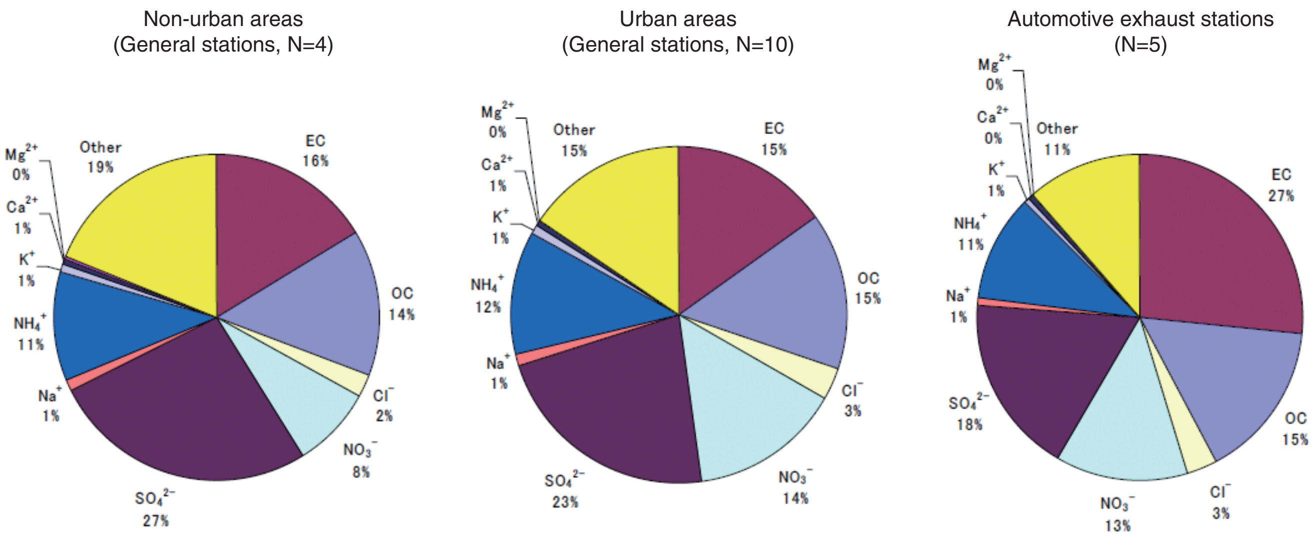
costs can be reduced. Based on the above, we developed a collection filter and dehumidifier.

Development of a filter (TFH-01) for collecting PM2.5

In terms of the material properties of the filters that are generally used, there are glass-fiber filters and Polytetrafluoroethylene (PTFE) filters. With glass-fiber filters, the physical strength is strong but the density is large, and these have the material property of absorbing moisture, so the filter itself ends up absorbing moisture, which absorbs β-rays. This can generate large errors in the measurement values. On the other hand, PTFE filters have fewer moisture effects than glass filters, but they do have electrification, and which means that workers need to be careful when handling the filters during weighing. In addition, PTFE filters have weaker strength than glass-fiber filters, so the filters themselves can get warped, resulting in measurement errors, so there is a problem where if support is provided so that the filters don't warp, the β-ray permeation amount decreases. As such, we developed a filter (Figure 3) with a two-layer structure with PTFE and non-woven fabric that combines both low hygroscopicity, which is a characteristic of PTFE, with the strength of the glass fibers, which makes it possible to minimize the effects of strength and humidity. Furthermore, by making the filter thin, we were able to decrease the minimum limit for detection by approximately 2 times that of conventional glass-fiber filters. The results of readings while filtering air that does not contain particles (no load test) are shown below. (Figure 4)

Development of a dehumidifier

The typical components that make up PM2.5 are shown below. (Figure 5) Many PM2.5 particles consist of gaseous sulfuric acid and nitric acid through photochemical reactions and absorbing water vapor from the air and secondary organic aerosol, Sulfur Dioxide



※Other: Mass concentration with carbon and ion concentration subtracted

Figure 5 component composition Source: 2007 Research Report on the Effects of Exposure to Fine Particulate Matter

(SO_2) or Nitric Oxide (NO) discharged from sources and secondary inorganic aerosol particulized due to reacting with Ammonia (NH_3) in the air. Here, "secondary organic aerosol" refers to particles that were particulized because of Volatile Organic Carbon (VOC) in the air condensing to a substance with low steam pressure due to a partial photochemical reaction. Due to photochemical reactions and absorbing water vapor from the air, these exist as gaseous sulfuric acid and gaseous nitric acid, but there are inorganic secondary product particles that were particulated due to reacting with NH_3 in the air. Out of these, ammonium sulfate and ammonium nitrate are deliquescent and absorb moisture due to relative humidity, which affect the measurement values. For that reason, with APDA-375A, we developed a heater to heat the air samples, which decreases the effect that changes in relative humidity have on the measurement values.

Current Status of Countermeasures against PM2.5 and Related Issues

Since PM2.5 environmental standards were set in FY2009, as of the end of FY2013, mass concentration has been continuously monitored at a total of 859 stations. During FY2012, the air pollution monitoring stations reported that only 43.3% of the environmental standard was achieved, and the motor vehicle exhaust monitoring stations reported that only 33.3% if the environmental standard was achieved, and effective countermeasures are being required. During last year, the current status with regard to the primary particles (dust and soot, coarse particulates, particulate substances (exhaust gas emissions from automobiles), etc.) that are sources that generate SPM and PM2.5 is that they have been reduced significantly, and these results have been confirmed. However, there is insufficient knowledge about the behavior of secondary particles that come from gases that many PM2.5 particles contain, which are discharged and then particlize to create secondary particles. For that reason, the work processing standard revised by the Ministry of the Environment requires that PM2.5 components be analyzed in addition to mass concentration, which makes it possible to clarify the countermeasures against the sources generating the particles as well as the mechanisms for generating the particles, and also to use the continuous measurements to check the trends over time and the results of the countermeasures. However, the Fine Particulate Matter (PM2.5) Component Analysis Guidelines (July 2011) limit the sample collection points (number of points) and the number of measurement cycles (about two weeks in each of the four seasons, spring, summer, fall, and winter), and the work of analyzing the collected particle requires specialist knowledge and experience, which results in the problem where these measurements take a lot of time and cost money to implement. For that reason, the current status is that it is possible to get an understanding of trends, but it is extremely difficult to do things like clarify the countermeasures against the sources generating the particles and clarify the mechanisms for generating the particles.

HORIBA's Activities and Countermeasures against PM2.5

A filter could handle analyzing the components

We have explained that it is important to analyze the components in making PM2.5 filter countermeasures. For that reason, in addition to the countermeasures for the PM2.5 low-concentration measurements, it was necessary to achieve a filter that could handle analyzing the components, which was important in researching future PM2.5 countermeasures and health effects. The conventionally used glass-fiber filters contain many impurities, and it has been difficult to analyze the components of the collected particles, but the filter we developed uses a filter material with few impurities, which made it possible for us to analyze the components. This filter is also used for APDA-375A, and this will allow us to not only measure mass concentration, but to also use it as a sampler for analyzing components.[*3] Table 3 shows the results of analyzing the components of the filter itself. In water-soluble component analysis, the components were put into a 15-ml polypropylene tube, and an ultrasound device was used to extract 10 ml of ultra-pure water (specific resistance: 18.2 MΩ/cm). When doing ion chromatography analysis, we filtered the extracted fluid with a nitrocellulose membrane filter (DISMIC-25CS, 0.45 µm, ADVANTEC). To measure positive and negative ions, we used a Metrohm IC 850.

When analyzing the components of inorganic elements,

Table 3 Water-soluble components remaining in the filter

Ions	Average ± σ	Ions	Average ± σ
F^-	ND	Na^+	23.6±13.8
Cl^-	15.0±5.2	NH4$^+$	ND
NO_2^-	45.6±34.0	K^+	ND
Br^-	ND	Mg^{2+}	4.0±0.6
NO_3^-	23.6±13.8	Ca^{2+}	36.9±2.9
PO_4^{3-}	ND		
SO_4^{2-}	5.7±0.57		

Unit: ng/cm^2

ND: Not detected. Text in italics indicates that the value is above the lower limit for detection and below the lower limit for quantification. Averages/standards are based on 5 sets of readings.

Table 4 Organic and inorganic element components remaining in the filter

	Average ± σ		Average ± σ		Average ± σ		Average ± σ
Li	<	Ti	<	Ge	<	Sn	0.19±0.02
B	<	V	<	As	<	Sb	<
Na	13.84±9.23	Cr	<	Se	<	Cs	<
Mg	13.26±1.61	Mn	0.02±0.01	Rb	0.01±0.00	Ba	<
Al	8.07±1.85	Fe	1.27±0.63	Sr	<	La	<
Si	18.45±4.27	Co	0.01±0.01	Y	<	Ce	<
P	ND	Ni	<	Zr	<	W	<
K	<	Cu	<	Mo	<	Pb	<
Ca	20.18±2.36	Zn	<	Ag	<		
Sc	ND	Ga	<	Cd	<		

Unit: ng/cm^2

ND: Not detected. Text in italics indicates that the value is above the lower limit for detection and below the lower limit for quantification. Averages/standards are based on 5 sets of readings.

we put the filter sample into a 15-ml polypropylene container, added 10 ml of 1% nitric acid solution to this, used an ultrasound device for irradiation, applied heat using a heat block, and broke down and extracted the inorganic elements from the filter sample. Then, we took the fluid where we had broken down and extracted the inorganic element components from the filter sample, poured it directly into an Inductively Coupled Plasma Mass Spectrometer (ICP-MS), and analyzed the element components. The ICP-MS we used to analyze the element components was the Agilent Technologies 7700x.

*3: The collection method for APDA-375A was not in accordance with the fine particulate matter collection method for measuring components that is listed in the Ministry of the Environment's Manual for Measuring Fine Particulate Matter Components in the Air (PM2.5).

Figure 6 PM2.5 automatic component analyzer

Potential for an Automatic PM2.5 Analyzer combined with X-ray Analysis Technology

By incorporating a fluorescent X-ray analysis device (MESA-50) that can measure the inorganic elements in PM2.5 into the APDA-375A, we have been researching a device (Figure 6) that can measure both the mass concentration and inorganic elements in PM2.5 using one unit. As such, although there was not much contribution to mass concentration, inorganic elements are extremely important as index components of the source. Because it is now possible to measure things like sulfur dioxide and nitrogen oxide in the same one-hour value (Figure 7), we expect that source analysis using the Chemical Mass Balance (CMB) method and Positive Matrix Factorization (PMF) method will play a part in analyzing particle sources.

Conclusion

Currently, air pollution problems such as PM2.5 are wide-ranging problems that go beyond national borders, and

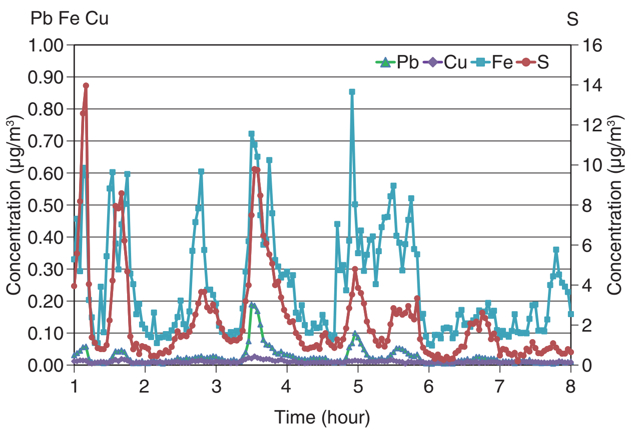


Figure 7 Results for measuring 1 hour of filtration (example)

Asian nations recognize these as common issues. To create effective countermeasures against PM2.5, it is becoming important to do detailed analysis, not just of mass concentration. HORIBA is developing an analyzer and measuring device for the automotive, environmental, scientific, semiconductor, medical, and other fields. We intend to work toward the conservation of the global environment and the development of the industry by successfully combining these analysis technologies to provide opportunities to solve these problems.

Reference

[1] Annual Report on the Environment in Japan 2014.

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