APPLICATION OF PARTICLE ANALYZERS TO ENVIRONMENTAL MEASUREMENT

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The PT1000 particle analyzer system that analyzes particulates using helium microwave-induced plasma can simultaneously measure the three-dimensional status of particles, composition and size of individual particles without requiring any preparatory treatment. the PT1000 has already achieved great results with applications to identify the source of dust generation in a clean room and to evaluate engineering materials such as toner particles. Applied to the field of environmental science, the PT1000 enables the source of airborne particles to be analyzed and the constituents and compositions of contaminants in soil to be structurally identified. Many expect that this system will allow pollution status to be analyzed and the source of pollution to be identified as well as their processes to be elucidated.

This paper describes examples of analyses with the PT1000 to measure suspended particulate matter (SPM) in different areas, to measure environments inside and outside housings, and to analyze heavy metals contained in soil. This paper also describes the possibility of using the PT1000 in applications for measurement related to the environmental regulation SPM2.5 that will be enforced in a few years.

INTRODUCTION

In the field of pollution measurement, conventional methods have been widely used to measure pollutants in the natural world. On the other hand, in line with recent focus on global environment issues, demand for the development of novel methods for environmental research has intensified. Suspended particulate matter (SPM), for example, has drawn public attention as a source of local air pollution problems. Subjects included in the scope of pollution measurement range widely, from problems concerning distant-transported acid particles to behaviors of the surfaces of particles in the stratosphere. What is important here is the need to reliably measure the composition, size and shape of particles in the environment and clarify the process in which the particles are produced and transported.

The PT1000 particle analyzer system[1)] is a system for

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Figure 1 External View of the System

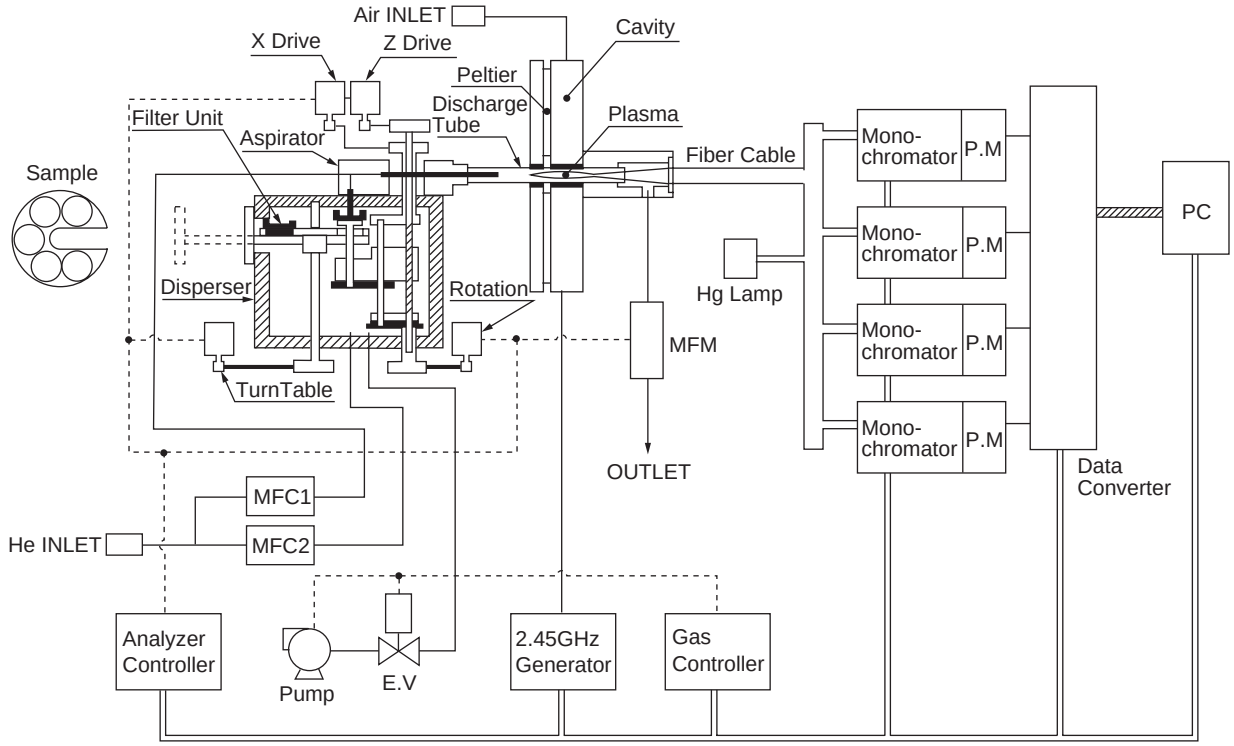

Figure 2 Block diagram of the System

analyzing particles using a microwave-induced plasma (MIP). More specifically, the system is the world's first direct analysis system that can introduce particles collected onto a filter directly into a plasma, one particle at a time, and analyze the constituents, composition and size of each particle at the same time. This system can be applied to the field of environmental studies to investigate the origin of airborne particles or determine the chemical combination of soil contaminants. Thus, much attention is now focused on the system in view of such applications as analyzing the state, identifying the source and clarifying the process, of pollution.

SYSTEM CONFIGURATION AND OPERATING PRINCIPLE

1. System Configuration

Figure 1 shows an external view of the system and Figure 2 illustrates the system's block diagram.

A few micrograms of sample particles are first collected by a dedicated sampler onto a 1-inch wide filter. The particles are then drawn up from the filter by an aspirator using helium as the carrier gas. Next, the particles are deflocculated within the sonic velocity region of the aspirator and introduced directly into a plasma, one particle at a time. A plasma emission unit provides a 150-W, 2.45-GHz microwave using a Beenaker cavity (electromagnetic resonant cavity)[2] having the resonance mode TM_{010}, thereby producing an atmospheric pressure helium plasma. The electron density and plasma excitation temperature at this point are reported to be 5.8×10^{14} electrons/cm^3 and 3600 K, respectively. The particles that entered the plasma are atomized, ionized, and then excited. The emission spectrum resulting from this excitation enters four spectrometers through optical fiber, where the spectra are processed with a time resolution of 90 μs. Consequently, we can determine the elements from emission wavelengths, the number of particles from the number of emission times, and the particle size from emission intensity. Furthermore, we can know the composition of the particles from the simultaneity and wavelength of emission. These data items are transferred to a workstation via communication. Each component of the system is controlled by the workstation so that all measurement tasks are done automatically.

One of the primary features of the system is the direct introduction of particles into a plasma. This feature not only eliminates the need for sample preprocessing but also makes it possible to characterize particles, one by one, to a total of a few thousand pieces. Another primary feature is the use of an atmospheric pressure helium plasma. The atmospheric pressure helium plasma has high excitation energy and, theoretically, can excite all of the existing elements. This means, the system can also analyze the halogens and lightweight elements with high sensitivity for which neither fluorescent X-ray radiation nor ICP emission will provide satisfactory levels of sensitivity.

2. Synchronous Emission and Equivalent Particle Size

Figures 3a and 3b show the ways a particle that is drawn through a nozzle emits light. There is no correlation between the emission signals A and B if the elements A and B enter into the

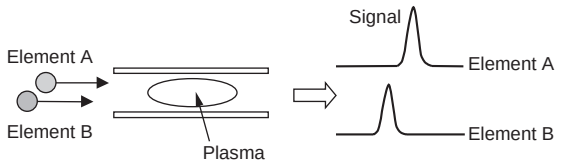

Figure 3a Emission from Separate Elements

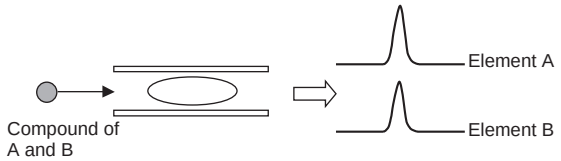

Figure 3 Emission from Compound

plasma as separate elements, as shown in Figure 3a. In contrast, In contrast, if the elements A and B enter into the plasma at one time, we can know that the emission is from compound of the two elements. By examining the simultaneity of emission, it is possible to determine whether the particle under test is a compound or separate elements. Applying this principle will enable us to determine the composition of SPM in air or heavy metals in soil. The intensity of emission is represented as an equivalent particle size on the assumption that each element is truly spherical and single-component.

ENVIRONMENTAL MEASUREMENT CASE STUDIES

1. Measurement of Suspended Particulate Matter (SPM) in Air

In this section, we will discuss examples[3)] of analyzing suspended particulate matter (SPM) in air. In the past, it used to take a week or two to sample SPM for chemical analysis or other purposes. PT1000-based analysis, on the other hand, allows us to reduce the sampling time dramatically since it requires only a marginal amount of samples.

Figures 4 and 5 show the results of measuring SPM samples collected using the LV1000 (low-volume sampler) over a period of approximately 20 minutes in three locations—urban areas of

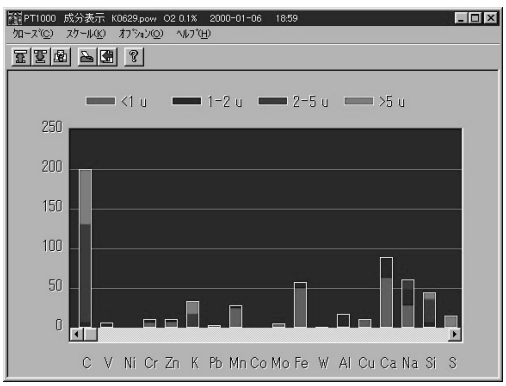

Figure 4 Components Window of PT1000 for Kiyosato Sample

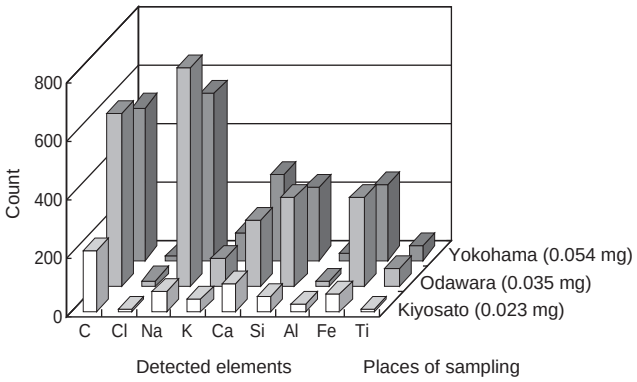

Figure 5 Relationship between Areas and SPM Samples

Yokohama and Odawara and in the mountainous area of Kiyosato. Figure 4 shows the Components window of the PT1000, where the X axis is the elements and Y axis is the count of particles detected. Figure 5 is a diagram of comparison among the areas regarding the count of each element detected, where the X axis is the elements, Y axis is the area and Z axis is the count. Judging from these figures, we can say that the mountainous area of Kiyosato is characteristic of low particle counts and, therefore,

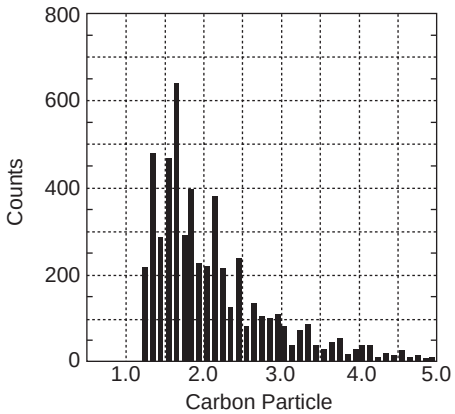

Figure 6a Carbon Particle Size of Odawara Sample

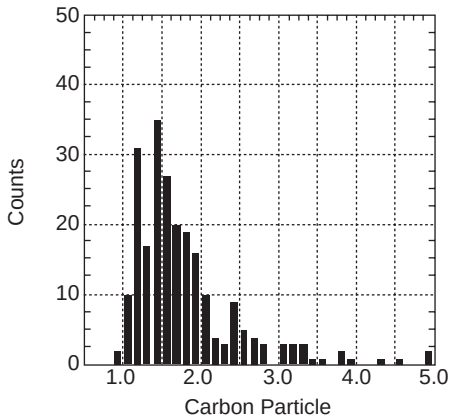

Figure 6b Carbon Particle Size of Automotive Exhaust Gas Sample

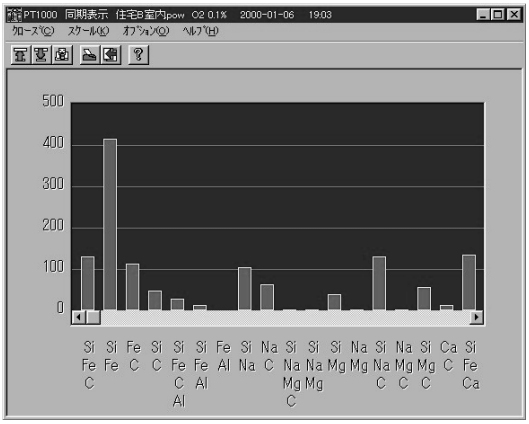

Figure 7 Compositions Window of PT1000 for Sample Taken Inside House B

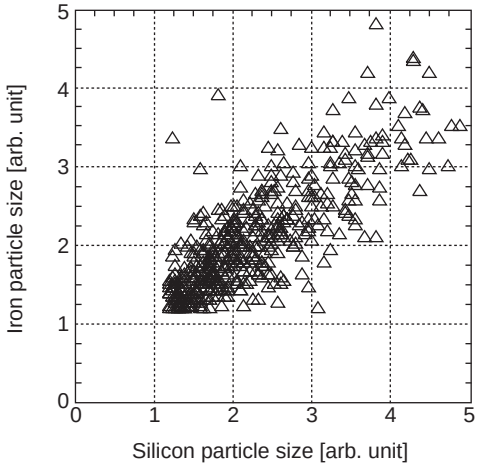

Figure 9 Relationship between Silicon and Iron Particles

environmentally cleaner than anywhere else. In contrast, high counts of carbon and sodium were observed in the urban areas of Yokohama and Odawara. We assume the carbon constituent is attributable to automotive exhaust gas, while the possible source of the sodium constituent is sea salt. This assumption is supported by the fact that as the result of comparison between Figures 6a and 6b, the distribution of carbon particle sizes in Odawara perfectly agrees with that of exhaust gas from diesel cars.

2. Measurement of SPM Indoors and Outdoors

Figures 7 and 8 show the results of measuring SPM sampled using the LV1000, over approximately 30 minutes each, inside and outside the house A in an urban area and inside and outside the house B in a suburban area. Figure 7 is the Compositions window of the PT1000 for an SPM sample taken inside the house B, where the X axis is the simultaneous constituents and Y axis is the count of particles detected. Figure 8 is a diagram of comparison among the locations regarding the count of each element detected, where the X axis is the simultaneous elements, Y axis is the places of sampling and Z axis is the count of particles detected. From these figures, we can understand that simultaneous silicon and iron constituents, which are soil constituents, are symbolically detected both inside and outside the house B in the suburban area surrounded by farms. We can therefore conclude that SPM of soil origin exists not only outside but also inside the house B. Figure 9 is a graphical output showing a relationship between silicon and iron emission spectra synchronously. The linear distribution of plots in the graph indicates that the ratio of chemical combination is constant and, therefore, the two constituents form a compound. In other words, the relationship between the silicon and iron constituents is almost linear, indicating that the iron constituent exists in the form of silicate mineral. Another point to note here is that large amounts of simultaneous silicon and magnesium constituents were found inside the houses A and B in common. This fact suggests that the particle in question stems from structural components of the house, such as asbestos.

Analyzing SPM in air using the PT1000 makes it possible to explicitly tell the difference in its properties according to the area

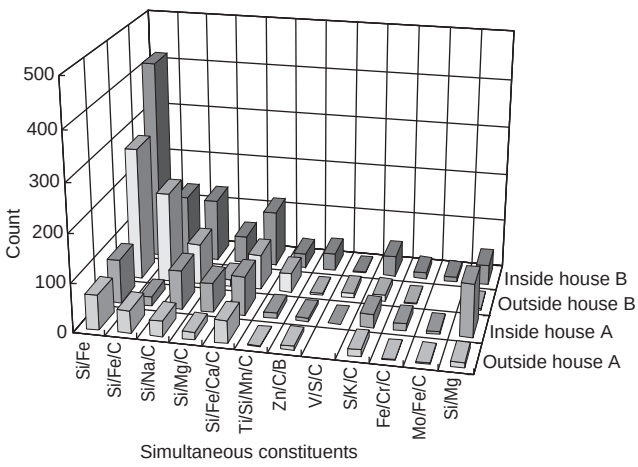

Figure 8 Simultaneous Constituents Inside and Outside Houses

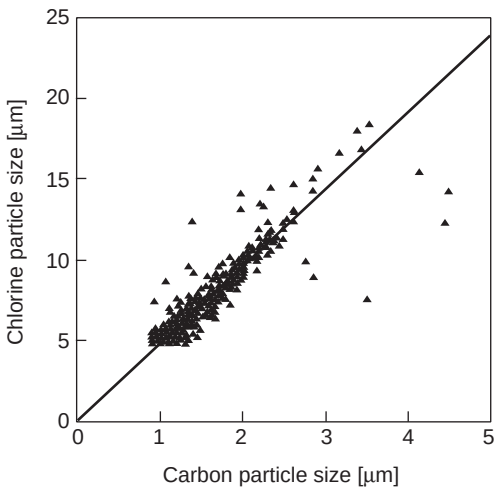

Figure 10 PCB in Soil

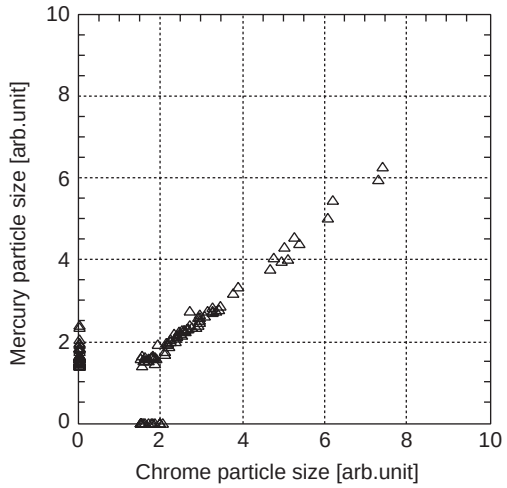

Figure 11a Mercurous Chromate in Soil

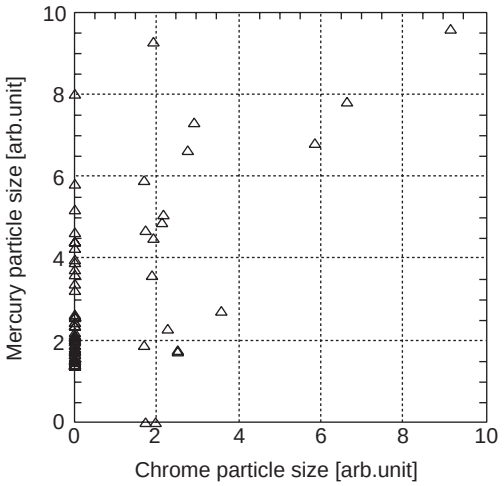

Figure 11b Mixture of Mercury and Chrome in Soil

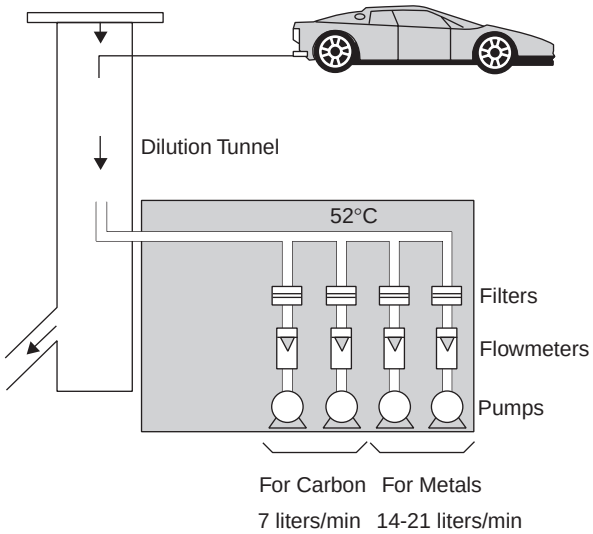

Figure 12 Sampling Method

or place of sampling. This feature is extremely useful for investigating the state and source of air pollution.

3. Examples of Soil Pollution Measurement

Figure 10 shows the result of analyzing PCB in soil[4]. The graph is the result of mixing PCB (Aroclor 1260) with soil and then analyzing the mixture, where the X axis is the carbon particle size and Y axis is the chlorine particle size. Although PCB is known to be a chemical compound consisting of carbon and chlorine, it is difficult to chemically identify this compound for reasons of its stability and composition. If PCB is submitted to analysis using the PT1000 system. We can find out correlation between emission spectrum of carbon and chlorine. Consequently, we can readily know that the carbon and chlorine exists in the form of a chemical compound. With the PT1000 system, it is possible to directly analyze PCB in this way.

Now, Figures 11a and 11b show the results of measuring samples prepared by mixing mercurous chromate (Hg_2CrO_4) with the standard soil specified by the National Institute of Standards & Technology and mixing mercurous oxide (HgO) and chromium oxide (Cr_2O_3) with the same standard soil alternatively. The X axis is the chrome particle size and Y axis is the mercury particle size. Mercury is a harmful substance and therefore must be removed from soil. The method of removal differs greatly, however, depending on the mode of mercury's chemical combination. It is therefore extremely important to know the mode of chemical combination of mercury contained in soil.

In the case of the sample soil containing mercurous chromate, the relationship between chrome and mercury is perfectly linear (Figure 11a). Mercurous chromate is a chemical compound characterized by an excellent regularity of distribution and, therefore, perfectly agrees with the linear characteristics noted above. Judging from comparison with the graph of silicate mineral shown in Figure 9, we can know that this relationship represents the combinatory state of the chemical compound. No evident relationship is found, however, when a mixture of mercurous oxide, chromium oxide and sample soil are measured (Figure 11b). Since chrome and mercury do not combine in the case of a mixture, the sample exhibits such an irregular distribution as shown in Figure 11b. As discussed above, the PT1000 system enables us to explicitly differentiate the mode of chemical combination between a mixture and a chemical compound, not to mention between pollutants.

4. Measurement of Automotive Exhaust Gas

Figures 13a and 13b show the relationship between carbon and iron in 13-mode driving test prescribed by the Japanese Ministry of Land, Infrastructure and Transport. Figure 12 shows the sampling method[5]. The X axis in Figure 13a is the driving mode and Y axis is the number of particles of the element detected. The notation of 60/40 means a driving mode with 60%

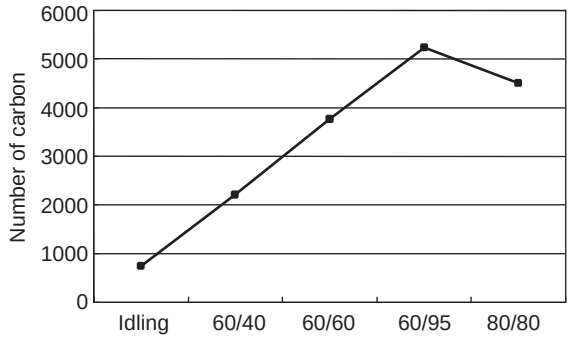

Figure 13a Relationship between Driving Mode and Carbon Particle Count

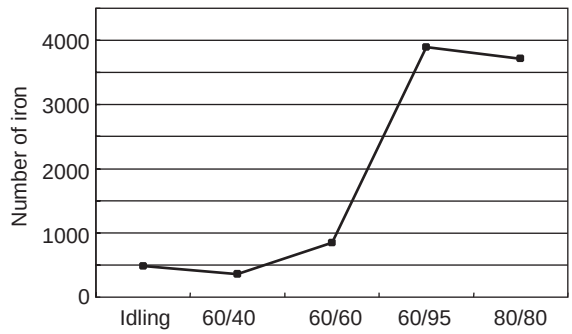

Figure 13b Relationship between Driving Mode and Iron Particle Count

of the maximum output power and 40% of the maximum load. A look at the number of detected carbon particles shown in Figure 13a indicates that the number increases as the load increases. This means, the quantity of carbon particles emitted varies depending on the magnitude of load, even if the output power is the same. More specifically, the amount of carbon emission increases almost linearly in proportion to the load.

A look at the result of measuring iron particles shown in Figure 13b, however, indicates that the graph is not linear with respect to the load. More specifically, the number of iron particles detected increases suddenly at a point beyond a specific threshold level. Since iron particles are assumed to result from the abrasion of an engine, it is anticipated that such abrasion begins suddenly when the load exceeds a specific threshold level. Accordingly, it is possible to know the relationship between automotive exhaust gas and driving mode, as well as diagnoze deterioration in the engine, by analyzing the exhaust gas.

CONCLUDING REMARKS

Effects of SPM or automotive exhaust gas in air upon the human body or environment will vary greatly, depending on the size and/or shape of particles contained in such SPM or gas. Despite this fact, the mainstream of conventional particle analysis methods has been microscopic analysis, such as particle size analysis and SEM analysis, or bulk analysis based on an ICP or atomic absorption. Thus, it wouldn't be quite right to say that we have been able to adequately analyze the impact of particles upon the real world of ecology.

We expect that the origins of fine particles will be identified and the process of production of such particles clarified by further promoting this research. Characterization of soil pollutants will become increasingly important for deciding methods for cleaning soil, and so will be research in this area.

With this system, we will explore environmental problems and clarify the process in which these problems occur and become wide spread. We hope these efforts will contribute to various industrial sectors, and toward the preservation of the global environment and the realization of a recycling-oriented society. ◆

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