Development of Direct Analytical Method for Gaseous Samples by Plasma Source Mass Spectrometer

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In recent years the spread of ICP-MS has been remarkable because of high equipment sensitivity and progresses in collision / reaction cell technology. However, direct analysis of gaseous samples is not yet possible because of the difficulty of maintaining plasma during direct analysis. We have developed a gas converter which can move particulate matter included in gas samples to argon in order to now make direct analysis of gas samples possible.

Using this new technology, real-time multi-element monitoring of airborne particulate matter samples was continuously examined by directly introducing an outdoor air sample via a PFA tube, and the signal intensities of 20 elements (40 isotopes) were measured at every 8 minutes for 80 hours. As a result, the signal intensities of Be, Ag, Cd, Sn, Sb, Tl, Pb, Bi, Th, and U were obtained at various instances.

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Introduction

The dissemination of inductively coupled plasma mass spectrometers (ICP-MS) has been remarkable in recent years. The range of use has rapidly broadened with increased sensitivity of the devices and the progress in collision reaction cell technology.1) In addition, it has become possible to directly analyze organic samples and individual samples because of the progress in auto-tuning functions and laser ablation technology,2) and there has been a dramatic improvement in the rapidity of analysis. However, in the analysis of outdoor air, gases for semiconductor materials and other gaseous samples, the metal components in the sample gas are typically collected in a filter, dissolved and are measured as an aqueous solution. They are easily contaminated during the operation, and a great amount of time and effort are necessary for the analysis. The reasons that direct analysis of gaseous samples cannot be done are that it is just difficult to maintain the plasma when the gaseous sample is introduced into the ICP-MS; the large volume of polyatomic ions that is generated causes spectral interference because of the composition of the sample gas; the plasma state changes, changing the ionization rate and accurate measurements cannot be made, etc.

The authors have developed a gas converter that makes the microparticles in the sample gas move to argon gas and have made it possible to directly analyze gaseous samples. Regardless of the composition of the sample gas, it is possible to make purer argon plasma measurements if this device is used.

On the other hand, the importance of aerosols has been recognized on various scales from the regional level to a global level. On the global level, aerosols are thought to play an important role in global warming and changes in precipitation, and in terms of regional problems, the secondary production of aerosols discharged as automobile exhaust gases and the waste gases emitted by factories into the atmosphere cause air pollution and are said to have a bad effect on health. In addition, while the expectations for nanotechnology to provide functions not possible up to now are expanding, there is a broadening opinion that it presents a risk to human health and the natural environment. According to a recent epidemiological survey, microparticles with a particle diameter of 2.5 µm or less contain many harmful components, and along with this, it is thought that they easily pass through the trachea, reach deep into the lungs and cause diseases of the lungs.3)

With this background, in addition to measurements using filter collection and ICP-MS described above, measurements with even higher temporal resolution (one hour level) using energy dispersive x-ray fluorescence spectrometers (EDX),[4] instrumental neutron activation analysis (INAA),[5], [6] particle induced x-ray emission (PIXE),[7] etc. are being carried out in Japan. However, since these methods collect the metal components in filters at the stage before measurements, there are many improvements, such as optimization of the filter materials for the method of analysis background improvements, that still need to be made in terms of reliability.

In addition, research on ICP-MS measurements,[9] etc., is carried out after measuring the composition of particles using an individual particle laser ionization mass spectrometer[8] and classifying the microparticles using a differential mobility analyzer. However, the smallest particle diameter that can be measured is large, and there are many problems that need to be solved for making devices practical, because the charge ratio is low for superfine microparticles.

The authors have directly introduced aerosols that are free in the outdoor air into an ICP-MS using the gas converter that they have developed and have examined the possibilities for real time simultaneous multi-element monitoring.

Gas Converter[10]

1. Structure and principles

For gas separation membranes used for the removal of the sample gas, there are porous membranes that give a propulsive force that diffuses the gas and non-porous membranes that make use of the affinity of the membrane and the gas. Since the components that can be removed by the latter are limited by the membrane material, the authors made a prototype of the gas converter using a porous membrane. The structure of the gas converter that was developed is shown in **Fig. 1**.

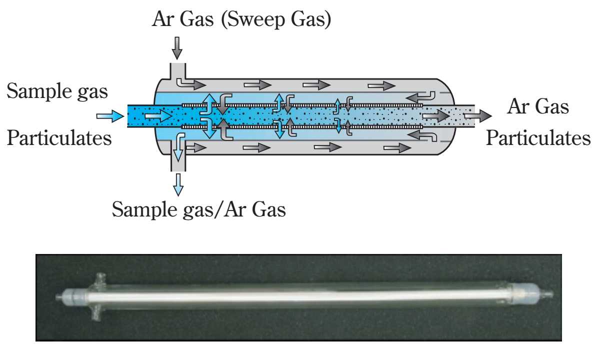

Fig. 1 Structure and a Photograph of a gas converter Apparatus

The sample gas that is introduced into the gas converter is defused in the argon gas (called the sweep gas) that flows in the counter flow direction on the outside of the membrane with the partial pressure difference on the inside of the membrane forming the propulsive force. Argon gas is defused on the inside of the membrane by the same principle, and as a result, argon gas flows out of the outlet of the gas converter. Since the rate of diffusion for the microparticles included in the sample gas is slow, they flow out of the gas converter with the argon gas. As a result, the microparticles in the sample gas can be moved into the argon gas.

The performance of the gas converter is controlled by the inside diameter, thickness, pore diameter and porosity of the membrane. For example, if the inside diameter is too small, the retention time is short, and if it is too large, it has a bad effect on diffusion in the direction of flow, lowering the performance. In addition, for reasons that will be described later, smaller pore diameters, within a range that does not affect the diffusion rate of the gas, are better, and the higher the porosity, the more the performance is improved. In designing the gas converter, it is necessary to optimize these conditions.

2. Performance

(1) Gas conversion rate

To find the gas conversion rate for the prototype gas converter, we introduced air as the sample gas and argon as the sweep gas and measured the nitrogen concentration in the gas at the outlet using chromatography. **Fig. 2** gives the results when using 450 mm and 600 mm porous long membranes with an outside diam-

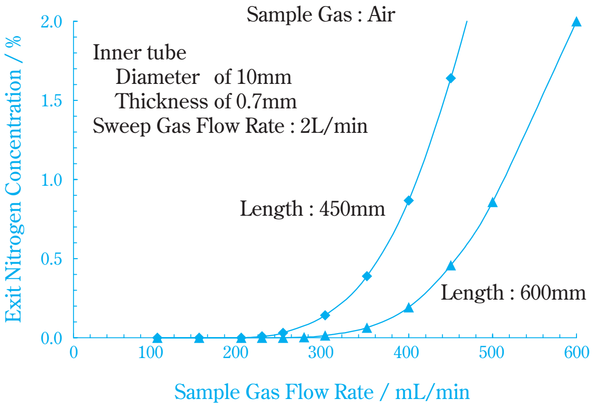

Fig. 2 The Influence of the Quantity of Sample Gas Introduction to give to Gas Exchange Efficiency

eter of 10 mm and a thickness of 0.7 mm for a sweep gas flow of 2 L/min.

From the results of the measurements, the concentration of nitrogen in the gas at the outlet is greatly affected by the flow of the sample gas, and it was 0.01% or less at 200 mL/min. with the length of 450 mm, and 260 mL/min. with the length of 600 mm. The longer the porous membrane was, the more it was possible to increase the sample gas flow.

(2) Evaluation using ICP-MS

When a gas sample is introduced into the ICP-MS, it is difficult to maintain the plasma, and this becomes more remarkable if the RF power is low. In addition, it causes an extreme drop in the sensitivity for the reasons previously described.

As an example, we will introduce the results of an experiment where nitrogen, carbon dioxide gas and 10% sulfur dioxide (N_2 balance) were introduced. In the experiment, the sample gas flow was a varied with an RF power of 1600 W, while a fixed amount of Mo was introduced into the ICP-MS using a standard gas generator for metallic elements. A diagram of the test device is shown in **Fig. 3**, and the results are shown in **Fig. 4**.

From the results of the experiment, the Mo ion intensity suddenly dropped because of the increase in the flow of the sample gas when either of the gases was introduced. This can be thought of as being the cause the plasma state changed because of the introduction of the sample gas; there was slippage from the optimal conditions for the device; charge mobility occurred, and argon ion density was reduced. In addition, sulfur dioxide generates a large amount of sulfur oxide ions in the plasma, and those are observed superimposed on various isotopes of Mo. In other words, the ion intensity that is measured is the sum of that for the ions of the Mo isotopes and the sulfur oxide ions, and since the size of that is proportional to the ratio of the isotopes of S and O present, we have m/z : 96 > 98 > 97 > 100.

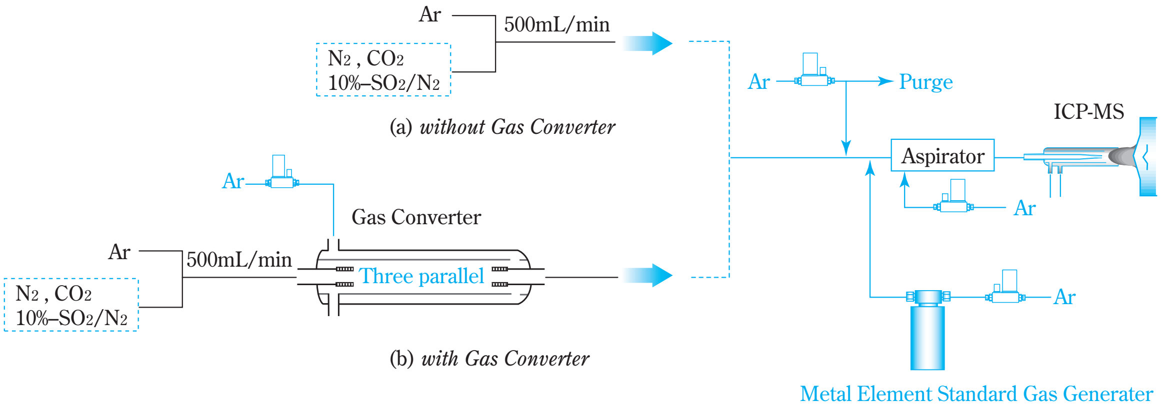

Fig. 3 An Example of Device which Used for Effect of Different Kinds Gas Introduction

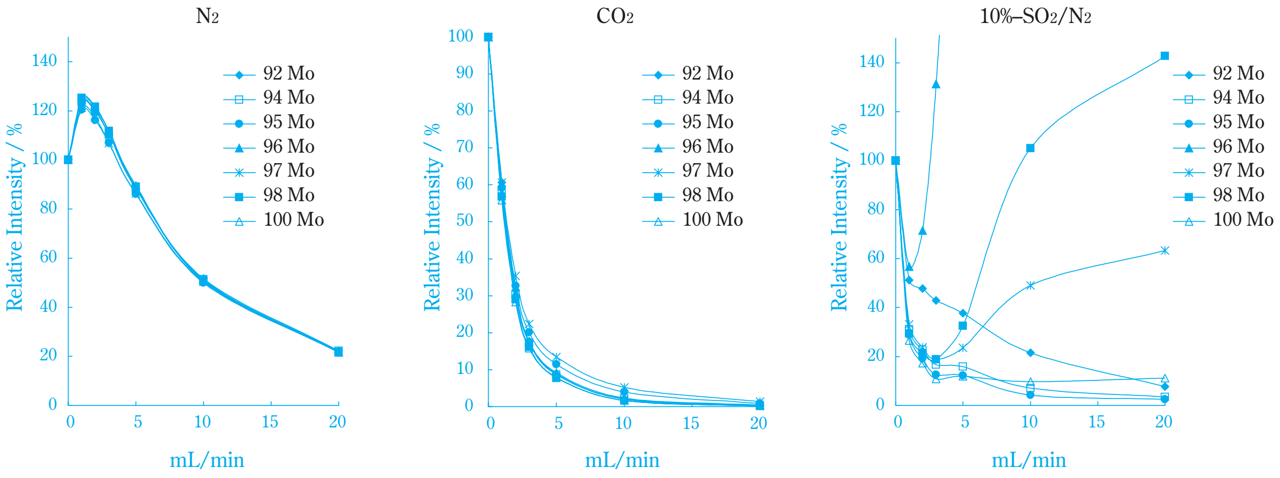

Fig. 4 Interference of Different kinds Gas Introduction

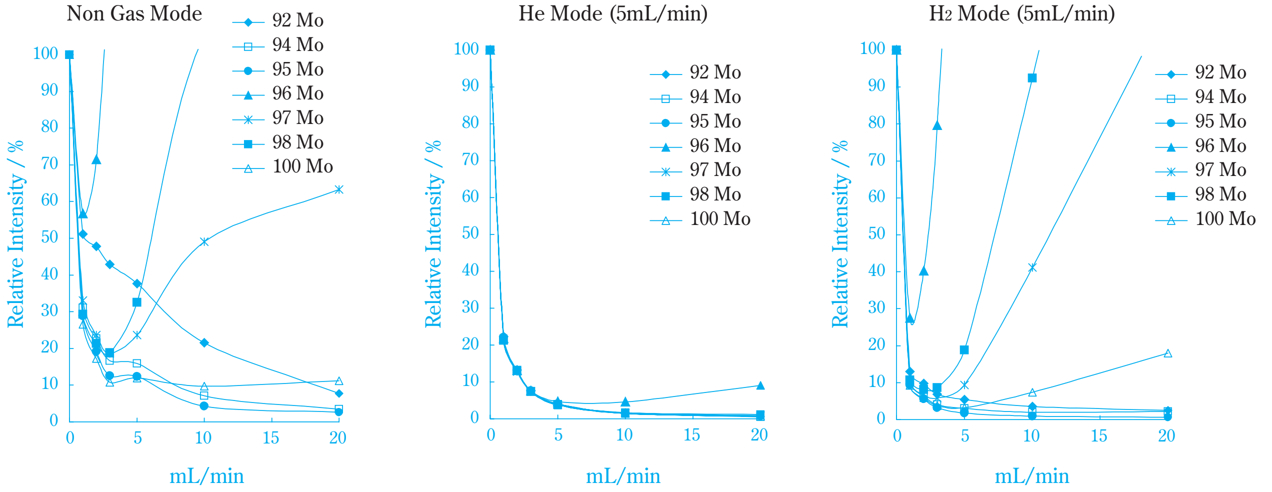

Fig. 5 Effect of Cell Gas (For Spectrum Interference)

Fig. 5 Shows the results when hydrogen and helium are introduced into a collision reaction cell for the purpose of removing the sulfur dioxide spectral interference (disturbance by the ions of sulfur oxides). The interference from the ions of sulfur oxide can be removed by the introduction of helium, but a sudden drop in the ion intensity cannot be avoided.

From Fig. 4 and Fig. 5, it can be seen that the proportion of the reduction in the ion intensity increases in the order of nitrogen < carbon dioxide gas < sulfur dioxide, and with sulfur dioxide, even if only the small amount of 0.1 mL/min. is introduced there is a sudden drop.

Fig. 6 shows the results for the gas converter, and the results were obtained by installing three gas converters in parallel and varying the sample gas flow rate up to 500 mL/min. Since the sample gas was completely converted to argon gas by the gas converter, the reduction in the ion intensity caused by the sample gas is eliminated, and no spectral interference due to sulfur oxides was found.

From these results, it can be said that removal of the sample gas before the plasma is introduced is the most effective.

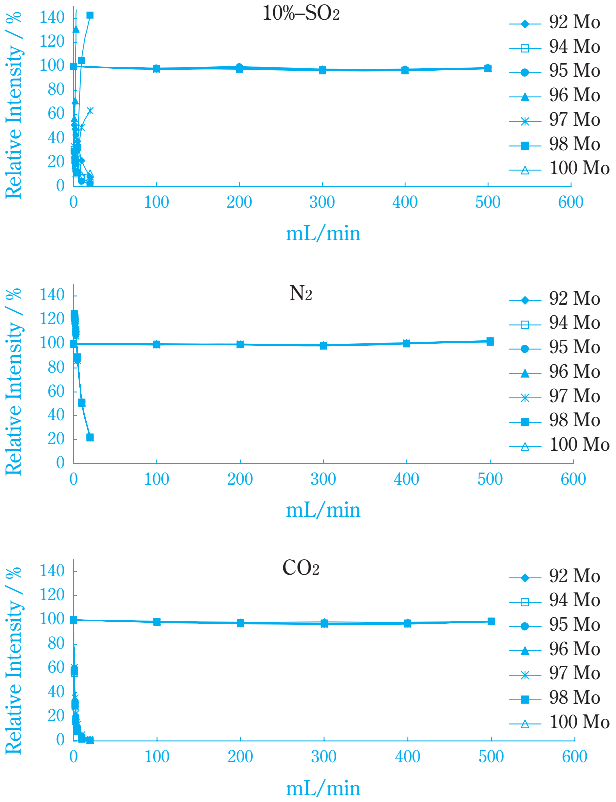

Fig. 6 Effect of A Gas Converter (For Interference of the Different Kind Gas)

Sample Introduction System[11]

Since the gas converter uses a porous membrane, a flow passing through the pores of the membrane arise is when a pressure difference is applied between the inside and outside of the tube. In addition, if there is a difference in the interdiffusion rates for the sample gas and the argon gas, the flow rate at the outlet of the gas converter changes.

Of these, the former can be improved by making the pore diameter smaller in the porous membrane as described previously. A sample introduction system that was proposed for the purpose of solving these two problems is made up of an aspirator and pressure equalization line as shown in **Fig. 7**.

If the ICP-MS and gas converter are connected, the increase in pressure that arises in the center tube of

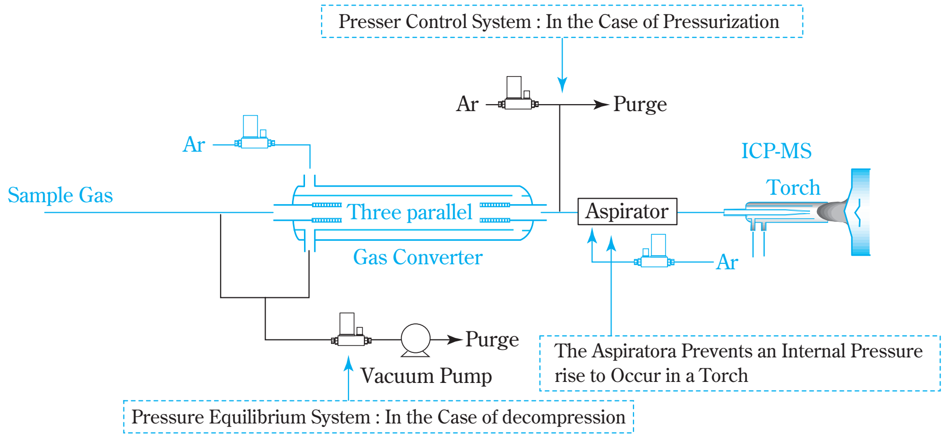

Fig. 7 A Figure of Constitution of the Sample Introduction System

the torch is transferred to the porous tube, but that can be prevented by using this system. In addition, in cases such as that where the sample gas is sucked in from a measurement point at a distance, etc., the pressure inside and outside the porous tube is equalized when the sampling line has a negative pressure.

Metallic Element Standard Gas Generator[12)]

In general, the optimization of measurement conditions for ICP-MS is carried out using a standard solution, so it is difficult to set the conditions for direct gas sample analysis using normal methods. The authors have developed a metallic element standard gas generator for the purpose of tuning the device and managing the precision.

As is shown in **Fig. 8**, the structure of the generator is one in which a cell encapsulating a solid having a slight sublimation pressure at normal temperatures and an argon gas flow path are linked by a capillary tube, and a mechanism is added to prevent gas from flowing in the capillary tube. The principles are extremely simple, and the diffusion inside the capillary to is rate determining for the amount generated. The concentration is determined by the temperature and the flow rate of the argon gas. Since the amount of the metal component that is generated is several hundred pg/min., it can theoretically be used for several tens of years.

Fig. 9 shows the results obtained with continuous introduction of the standard gas to an ICP-MS. The

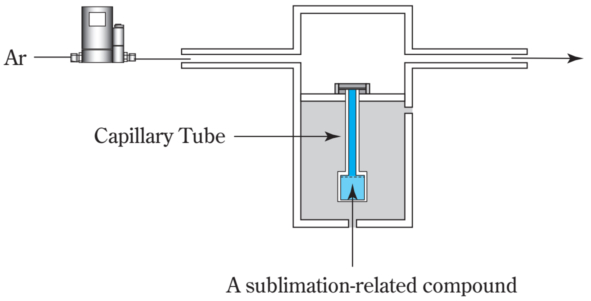

Fig. 8 The Structure of the Metallic Element Standard Gas Generator

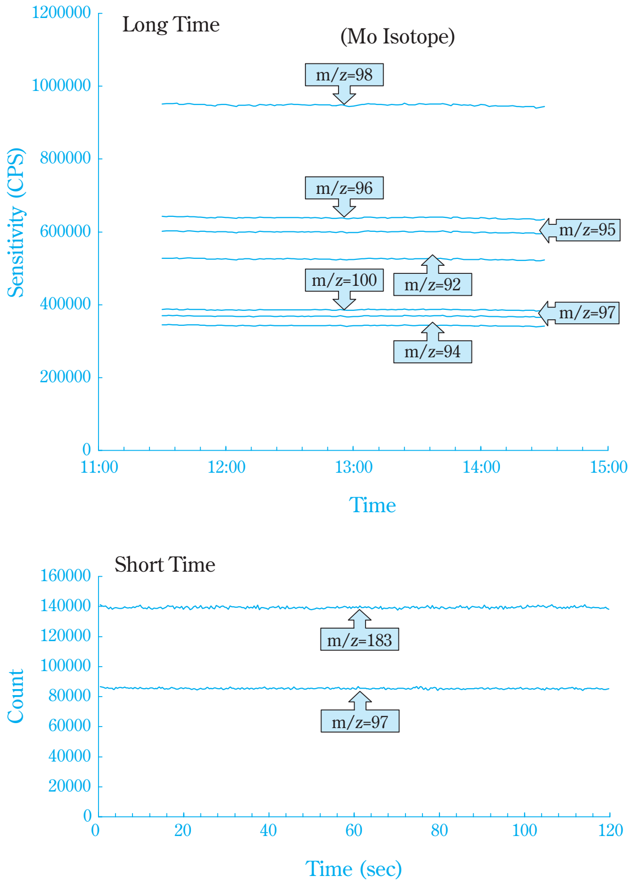

Fig. 9 Stability of the Standard Gas Concentration

long-term stability and the short-term stability are shown, and it can be seen that the concentration is extremely stable.

Increasing Analytical Sensitivity[13)]

There are two problems for direct analysis of gas samples, elimination of spectral interference caused by components coexisting in the sample and increasing the sensitivity, and in particular, increasing the sensitivity is extremely important because there is no concentration operation. For the former, elimination of gas components using the gas converter, use of collision reaction cell technology, use of high resolution ICP-MS, etc., are effective, but for the latter, no effective means other than increasing the performance of the device and optimization of the measurement conditions has been found.

1. Effect of introducing nitrogen

Since the plasma generated in this method is dry plasma, the plasma temperature is usually higher than that of the method for introducing the solution. The plasma ion density is increased by introducing a small amount of nitrogen, and as a result, we can expect an increase in sensitivity. **Fig. 10** shows the results of examining the effects of the amount of nitrogen introduced with RF power of 1600 W while introducing a fixed amount of Mo. The Mo ion intensity is greatly affected by the amount of nitrogen introduced and the sampling depth, and a seven to eight fold increase in intensity can be found with optimization of the amount of nitrogen introduced when compared with the case where no nitrogen is introduced. Based on the results of the experiment, the sampling depth and amount of nitrogen introduced were determined to be 8.5 mm and 7.0 mL/min.

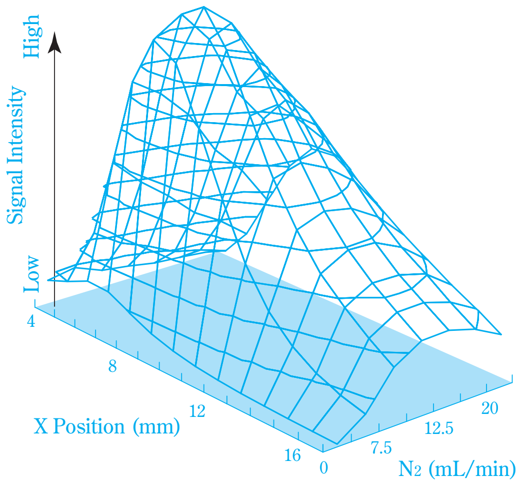

Fig. 10 Effect of Sampling Depth and Nitrogen Introduction

2. Combined use of cool plasma and cell gas

To optimize the measurement conditions for the Fe that undergoes ArO^+ spectral interference, the sampling depth and amount of nitrogen introduced were set at 21.5 mm and 22.5 mL/min. as a result of examinations of the optimal conditions at RF power of 600 W. In addition, the amount of helium introduced was set at 3.5 mL/min. from the data shown in **Fig. 11** for the optimization of the cell gas flow rate.

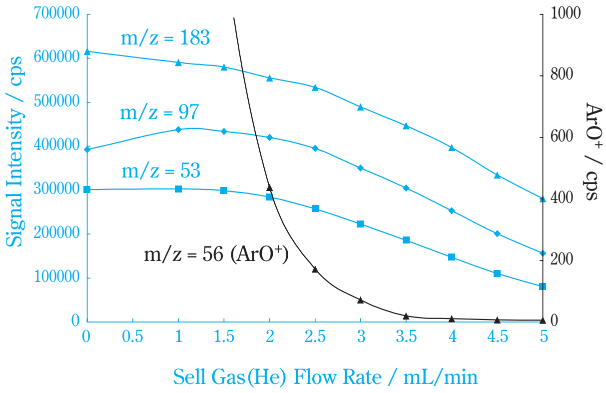

Fig. 11 Effect of A Cell Gas (Comparison with ArO)

3. Results of time analysis

In addition to increasing sensitivity by optimizing the plasma conditions, individual particles can be captured as a spike shaped signal in a time analysis, so we can expect improvements in sensitivity through this. As a result of a time analysis, which will be described in the following, the time for detecting (presence) of a single particle with ICP-MS is thought to be approximately 10 ms. If we assume that the time analysis of a sample gas where the concentration of individual particles is 1 particle per liter is done in an integral time of 10 ms, the amount of sample gas necessary for obtaining a single height equal to that of solution introduction is 12,000 m^3.

(Here the calculations were done for 50 mL of sample solution, a sample introduction rate of 0.5 mL/min. and a spraying efficiency of 5%.)

Therefore, with samples where the particle concentration is extremely low, such as those the air from a clean room environment, direct analysis (time analysis) is overwhelmingly effective.

Measurement of Aerosols in Outdoor Air13)–15)

Aerosols in the outdoor air were measured using the system shown in **Fig. 12** with the purpose of verifying the results of the investigations up to now.

The ICP-MS measurement conditions set the sample introduction flow rate at 600 mL/min. with the two conditions of

(1) RF power 1600 W (Hot Plasma)
(2) RF Power 600 W (Cool Plasma)

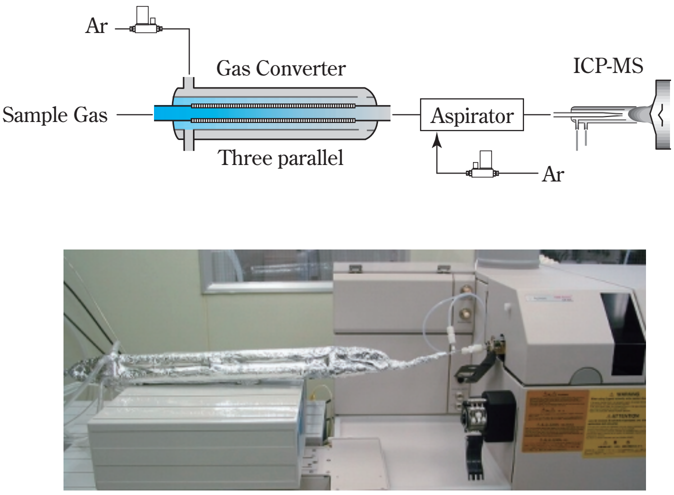

Fig. 12 Schematic Diagram and a photograph of Sample Introduction System

1. Example of time analysis

(1) Fe Measurements

The results of a time analysis for Fe in the outdoor air carried out using measurement condition (2) with an integral time of 10 ms with helium introduced as the cell gas at 3.5 mL/min.

The measurements alternately and repeatedly introduced the air from inside a clean room and outdoor air. The two graphs show the same measurement results with a different scale all on the vertical axis, and the lower figure is a 4000x enlargement of the upper graph. If even a little oxygen is mixed in, ArO^+ is generated, and it can be seen that the measurement of the Fe, for which the analysis becomes difficult, can be done with extremely high sensitivity even with the introduction of a large volume of air.

(2) Sn and Pb measurements

The results of time analysis for Sn and Pb in the outdoor air carried out using measurement condition (1) with an integral time of 10 ms are shown in **Fig. 14**. If the two measurement results for Sn and Pb are compared, the base in the results for Sn appears to be floating. This is thought to be because a large number of extremely minute particles are present. Therefore, to confirm the presence of superfine particles, clean air was used for the environmental air, and time analysis was carried out at delutions of 10, 100, 1000, and 10,000 times.

As a result, the base for the ion intensity every 10 ms with the 100x dilution dropped comparatively, and subsequently, the number of peaks with an ion intensity of approximately 100 dropped off proportionally to the

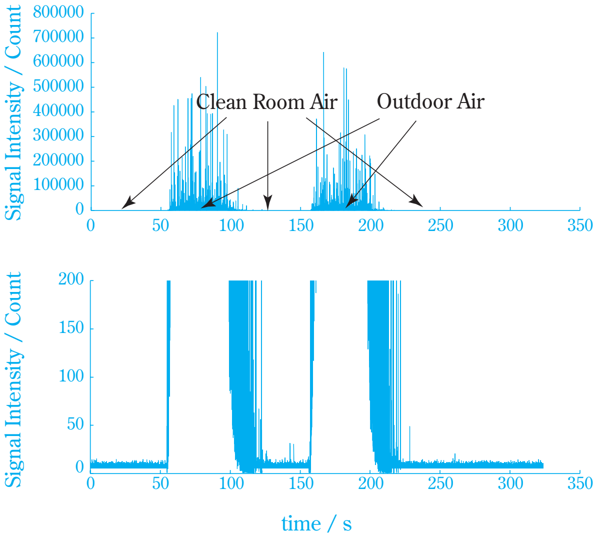

Fig. 13 Signal Intensity of ^{56}Fe in Cleen Room Air and Outdoor Air

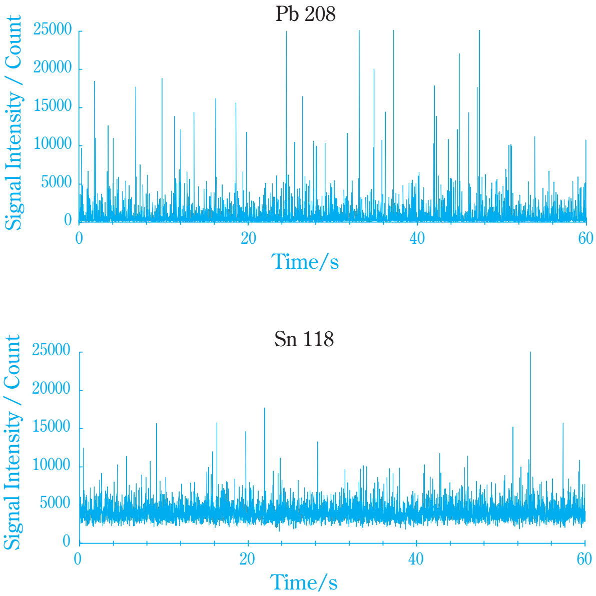

Fig. 14 A Measurement Result in Time Analysis of Sn and the Pb

rate of dilution. From these results, we could estimate that approximately 1000 particles per milliliter of minute particles containing Sn with an ion intensity of approximately 100 were present.

Therefore, direct analysis is quantitative in addition to giving the mass concentration of metallic elements, and information on the size of microparticles and the concentration in numbers can be obtained.

2. Example of monitoring

An example of the results of approximately 80 hour continuous monitoring of 20 elements in the outdoor using measurement condition (1) is shown in **Fig. 15** (measurements being taken at approximately 8 hour intervals).

From the results of the measurements, it can be seen that measurement of elements with tiny amounts such as U, Th and Be is sufficiently possible. In addition, elements thought to be of artificial origin, such as Sb, Sn, Pb, Tl, Cd, Bi and Ag are monitored by each of their patterns, and various types of information can be read from these patterns.

For example,

i) All of the concentrations of the elements change hour by hour, and the variations in the concentration of Tl are 2000 times or more, etc., so the temporal changes are extremely large.

ii) Elements for which the patterns match extreme-

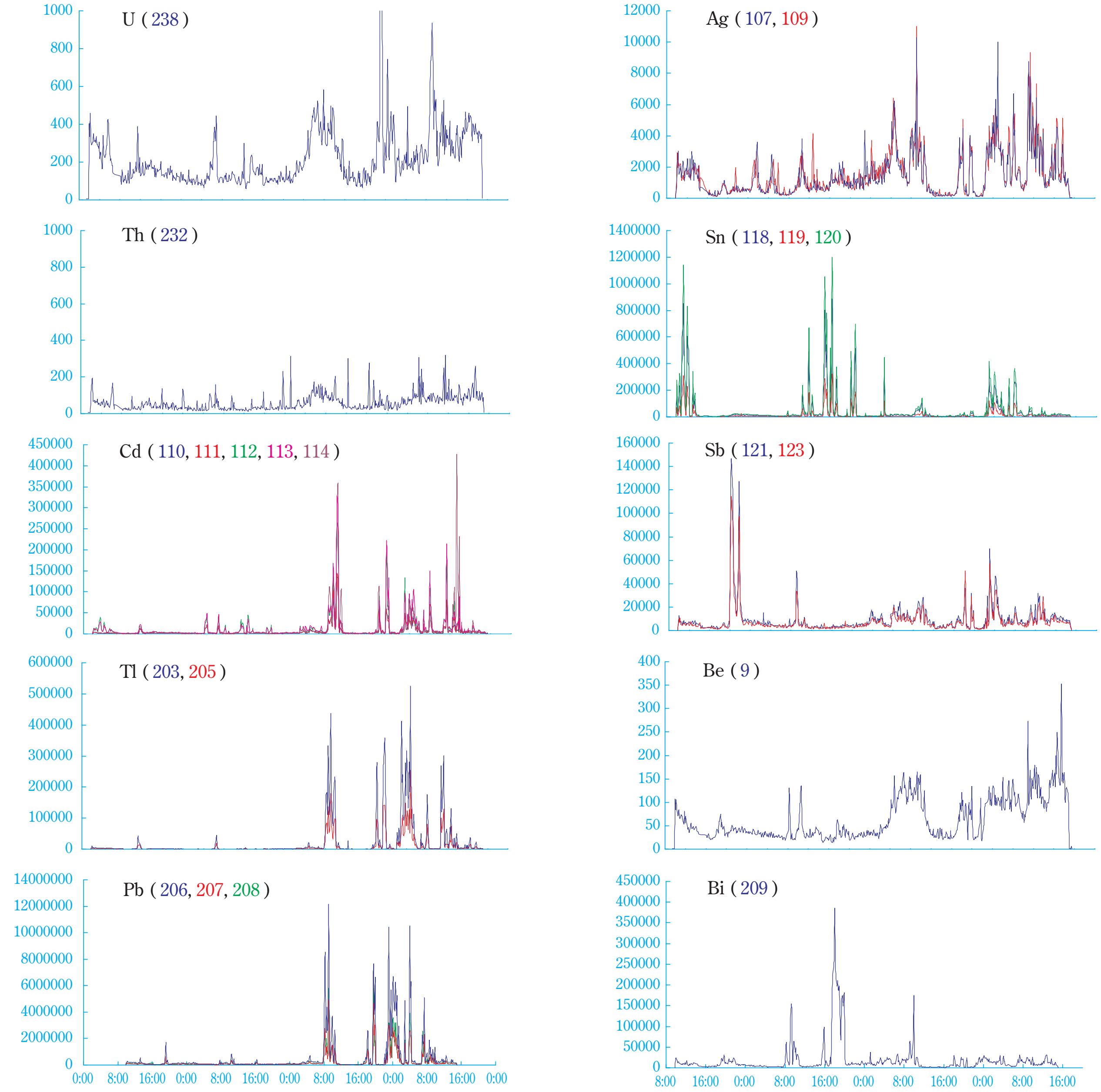

Fig. 15 Continuous Multielement Monitoring of Enviromental for 80 Hours

ly well, such as Pb, Cd and Tl are presumed to have the same source.

iii) Since the ratio of the concentration of U is higher when the concentrations of Th and U are compared with their rates of presence in the Earth's crust, it can be assumed that this is caused artificially by manufacturing activities, etc.

iv) The concentration distribution curve$^{13)}$ obtained by analyzing the data for Be shows clearly that to did distributions are superimposed, and that indicates the presence of multiple sources, etc.

In addition, the isotope patterns obtained for each of the elements matched well, and it was found that the reliability of the analysis was high because there was no memory effect before and after the monitoring.

As is seen from the results of these measurements, the concentrations of the aerosols in the air vary in temporal and spatial terms, and a measurement method with high temporal resolution is indispensable for clarification of their dynamics. The usefulness of this method was verified.

Conclusion

As has been discussed above:

i) Direct analysis of gas samples has been made possible. (By removing all gas components, it was possible to stabilize the plasma and eliminate spectral interference due to the sample gas.)

ii) By introducing a small amount of nitrogen, we could increase the sensitivity seven to eight fold.

iii) Real-time multi-element monitoring was made possible.

iv) It was possible to verify that this is extremely effective for clarifying the dynamics of aerosols in the outdoor air.

This technology was first made possible by using the gas converter, and not only outdoor air, but also various other samples can be used. In addition, if ICP-TOFMS and MCICP-MS are used, we think that direct analysis of the composition of microparticles in the gas sample and the isotopes will become possible. Going forward, we would be happy if this technology contributes to the development of plasma mass spectrometers and leads to a societal contribution through clarification of the dynamics of the environment of the air.

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