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## What Are We Breathing ? — Atmospheric Particles and Electron Microscopes —

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**Abstract :** Although many kinds of particles are floated in the atmosphere, no one has really attempted to definite experimentally what each particle originated from, or classify the particles by the origin. Therefore the observations of the smoke produced by the combustion of many types of materials were undertaken, and elements composing the burnt particles were analyzed by EDX, in order to interpret atmospheric particles. The structural difference of the major particles floated in the atmosphere can distinctly be seen in this report by both scanning and transmission electron micrographs. A range of experiments led to the result that atmospheric particles were classified into two categories according to their features. One can be identified as the spherical particles, 0.1  $\mu\text{m}$  in diameter, produced by the combustion of fossil fuel and petrochemical products. The elements of these particles were mainly composed of carbon. The other involves the particles produced by the combustion of plants. These particles, comparing to the former, were identified to be larger in diameter, and more various in both size and micromorphology. The elements of these particles were composed of a high concentration of silicon and aluminum.

*Key words :* Atmospheric particle, SEM, TEM, EDX, fossil fuel, petrochemical products, plants.

### 1. Introduction

While we breathe air to live, it is doubtful whether air we are just now breathing is safe or not. Presently smog is hanging over most of cities, and our health is gradually undermined by air pollution.

The particles involved in the atmosphere have actually been observed up until now. As an example, a large number of spherical particles, 0.1  $\mu\text{m}$  in diameter were identified by scanning electron microscope from the atmospheric particles collected at Matsue City from 19 to 24 December, 1991 (Fig-2, A). In addition film-like particles, 30 nm in diameter,

were observed by transmission electron microscope from snow that fell in Matsue City on 20 February, 1991 (Fig-2, B). Soot disclosed in these micrographs was identified to originate from a oil well blasted at Gulf War that broke out on 17 January, 1991 (Tazaki, 1992 ; Tazaki et al., 1992).

Atmospheric particles do not only come into being in special situations. As an example, over 50 % of suspended particulate materials sampled at Yokohama National University were identified to be sub-micrometer sized particles that contained a large amount of black carbon. This survey concluded that most of floating particles in the atmosphere were occupied by man-made (Arima et al., 1995). In addition, it was reported that such particles were developed from some gaseous substances by physical and chemical changes (Kasahara, 1988).

As described above, it is quite obvious that many kinds of particles are floated in the atmosphere surrounding us. It is observed that the amounts of the substances discharged artificially have been increasing year by year. The best example of such a substance should be acidic pollutants, the influence of which to the earth's ecosystem is so thoroughly being questioned. Especially nitrogen oxide (NO<sub>x</sub>) and sulfur oxide (SO<sub>x</sub>) produced by the combustion of fossil fuel is increasing world-wide acid rain or air pollution with unforeseeable effects on the earth (Watanabe et al., 1992). One of the fundamental causes of current environmental problems is considered to be the faulty circulation of carbon in which man-made combustions are involved (Tazaki and Takasu, 1994). Another report introduces the experimental results that diesel exhaust particles may be involved in the pathogenesis of lung diseases, including asthma and chronic bronchitis (Sagai, 1993 ; Nakajima and Kato, 1994). Furthermore, studies were undertaken for making floating particles experimentally, and observing mineral and carbonic particles in a car tunnel where high air pollution was examined (Miyata and Tazaki, 1995 ; Miyata et al., 1995 ; Miyata and Tazaki, 1996). The reports on distribution surveys that focused on degree of air pollution in a regular region, have been produced (Tazaki et al., 1995). There is another example that extracted opal phytolith from some living plants to observe them with optics microscope and analyze chemically with electron probe X - ray microanalyser (Inomata et al., 1995). However, there is no report that has experimentally confirmed the origin of each substance, and that has really analyzed substances for classifying according to the features of them.

Therefore, a range of experiments were carried out in order to observe the burnt particles of fossil fuel, petrochemical products, and plants with electron microscopes. The elements of each burnt particle were also analyzed by EDX for classifying the samples according to the results.

## **2. Samples**

### *2.1 Original Substances Used for Experiments*

The following thirteen types of the materials were available for observation and analysis ;

light oil (diesel), polyethylenes, newspapers, liquid petroleum gas, kerosene, coals, polystyrene, straw, vinyl chlorides, woods, charcoal, pampas grass, and gasoline.

## *2.2 Methods for Sampling*

Burnt particles of diesel and gasoline were obtained from the exhaust pipe of a diesel car and a gasoline car respectively, and were adhered to the surface of a sample stub for scanning electron microscope use. The samples obtained from the diesel car were observed on a microgrid with transmission electron microscope after once suspended with distilled water.

Polyethylenes, newspapers, coals, straw, vinyl chlorides, polystyrene, woods, charcoal, and pampas grass were burnt respectively in Shichirin, a Japanese stove. Smoke produced by burning was concentrated on a large cone chimney, designed to collect particles directly on the top with sample stubs for scanning electron microscope use, and with a microgrid for transmission electron microscope use. Situation of collecting samples is as Fig. 1.

Burnt particles of liquefied petroleum gas and kerosene were collected with sample stubs from the deposits on each core of a cassette gas stove for liquid petroleum gas (LPG) use and an oil heater for kerosene use.

So as to adhere the burnt particles easily, a piece of carbon double-sided tape had been put on all sample stubs prepared for the observations.

## **3. Methods**

The micromorphology and the size of each sample were observed by JEOL-JSM-5200 Scanning Electron Microscope (SEM) at an accelerating voltage of 15 kV. Elemental concentration measurements were analyzed by SEM, equipped with energy dispersive X-ray analyzer (EDX), a Philips-EDAX PV9800 STD model, at an accelerating voltage of 15 kV. Some samples were observed by JEOL-2000 EX Transmission Electron Microscope (TEM) at an accelerating voltage of 200 kV.

## **4. Results**

Scanning electron micrographs and transmission electron micrographs of each particle collected from the smoke produced by burning the materials respectively can be indentified as follows.



Fig. 1 Situation of collecting samples.

- 1 : Making a fire in "Shichirin ", a Japanese stove.
- 2 : Burning an original material in Shichirin to collect particles in smoke.
- 3 : Producing the smoke contained samples, which is concentrated on the top of a big cone chimney.
- 4 : Putting sample stubs for both SEM use and TEM use on the top of the chimney. Burnt particles are stuck on the surface of the sample stubs (showing with an arrow).

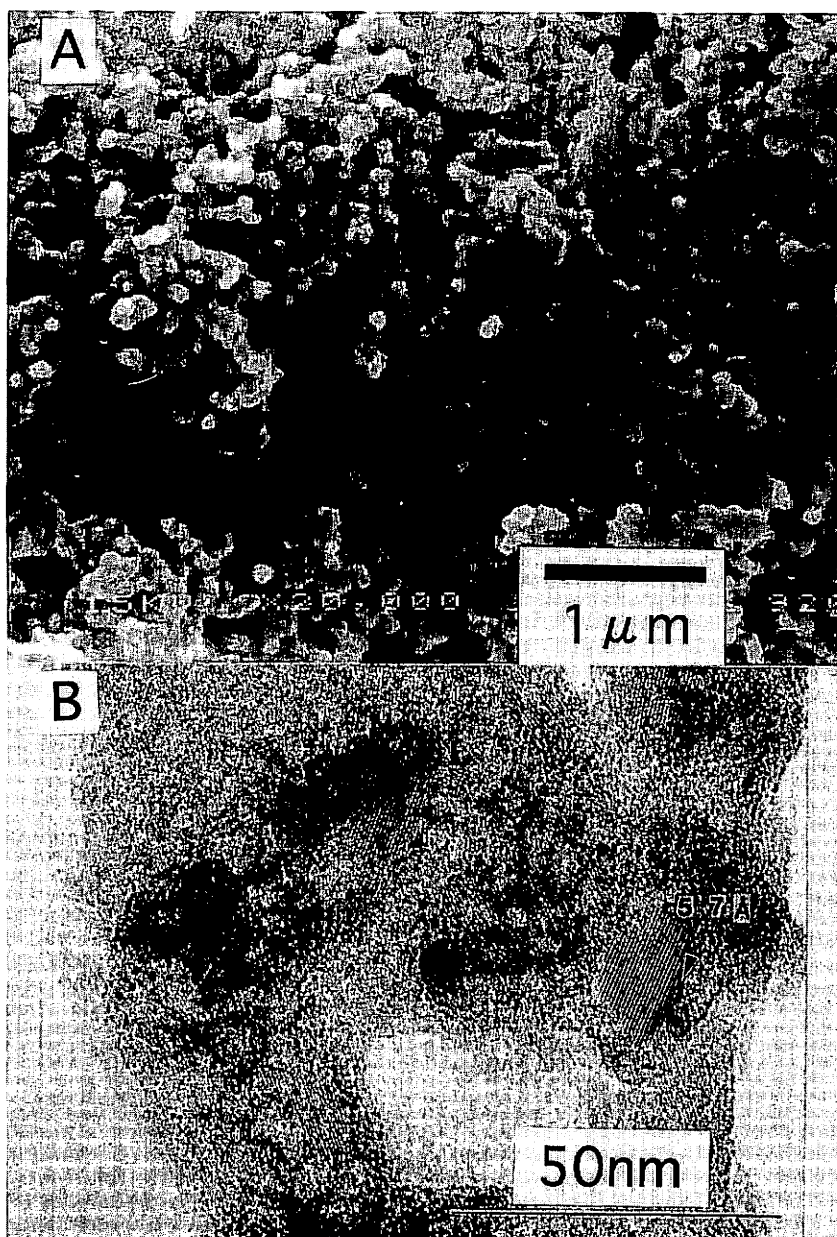


Fig. 2 Electron micrographs of soot produced at an oil well blasted at Gulf War that broke out in the Middle East on 17 January 1991.

- A : Scanning electron micrograph of the spherical particles,  $0.1 \mu\text{m}$  in diameter. The particles were found from the atmospheric samples in dusts floated over Matsue City from 19 to 24 February, 1991.
- B : Transmission electron micrograph of the coated particles of 30 nm in diameter. The particles were found in snow sampled in Matsue City on 20 February, 1991.

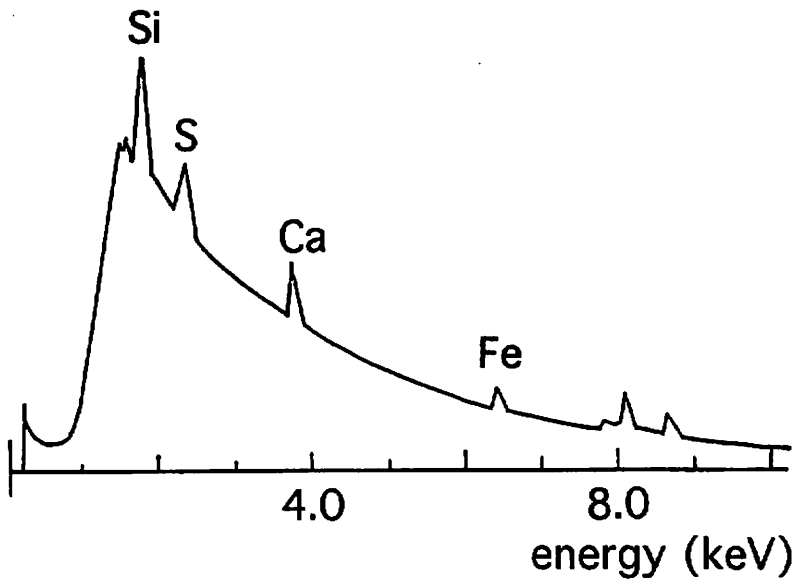
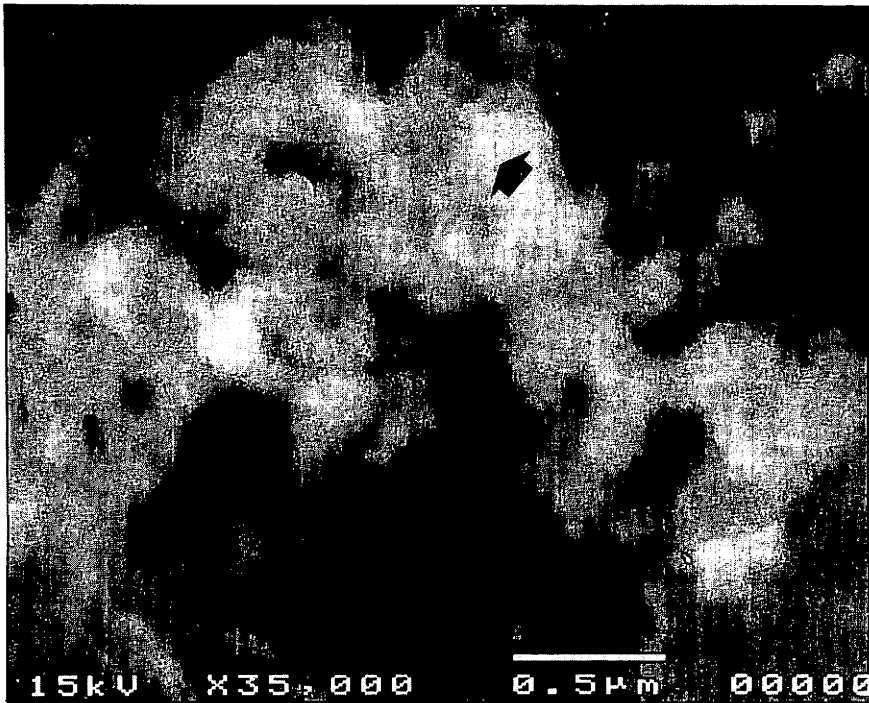


Fig. 3 Scanning electron micrograph and energy dispersive X - ray analysis of the fine particles in the material obtained from the exhaust pipe of a diesel car. Light oil is used for fueling diesel cars. The particle is about  $0.1 \mu\text{m}$  in diameter, and was observed as showing an arrow on the photograph. The major element of this particle is carbon.

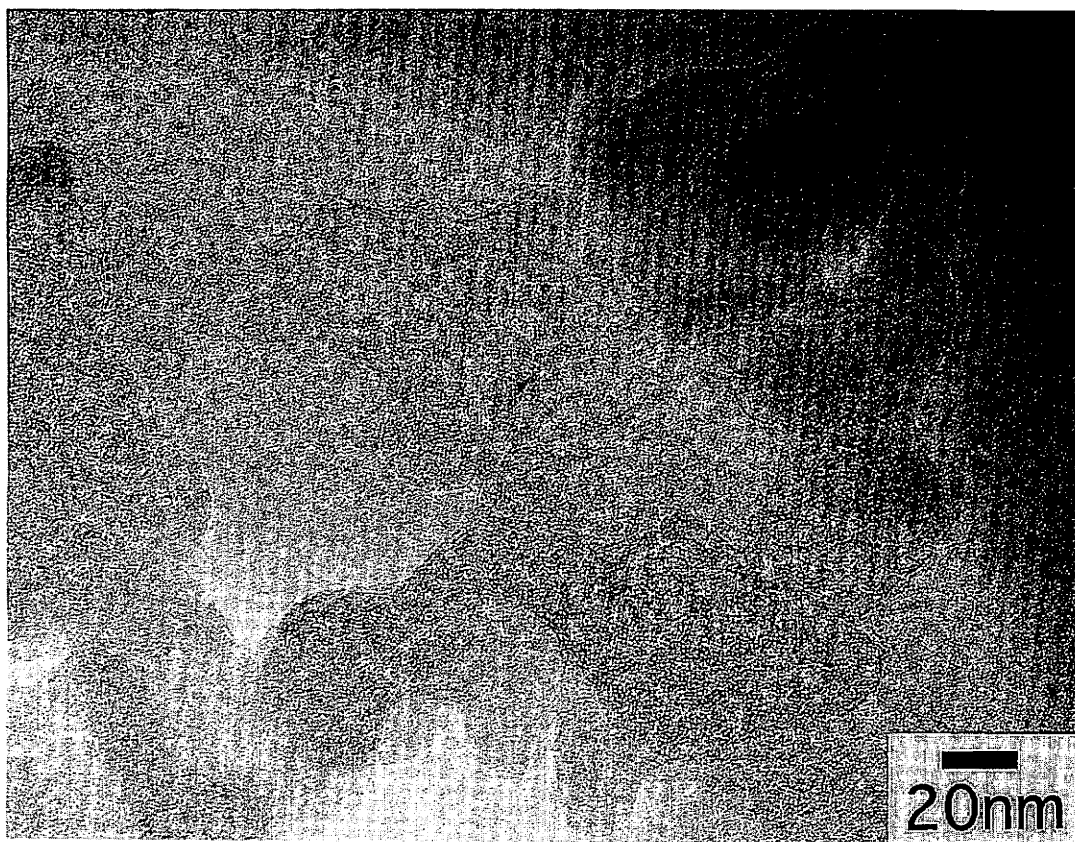


Fig. 4 Transmission electron micrograph of the fine particles in the material obtained from the exhaust pipe of a diesel car. Particles were not isolated, but were identified to be in connecting each other without clear boundaries.

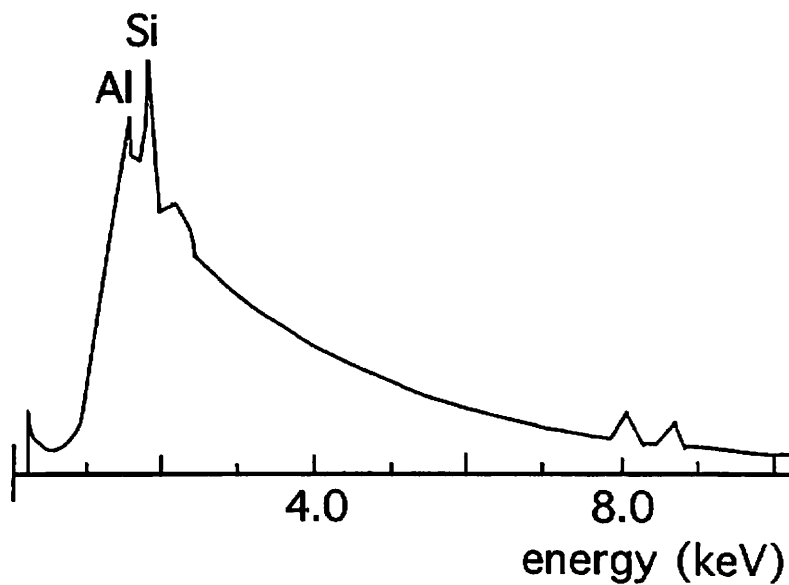
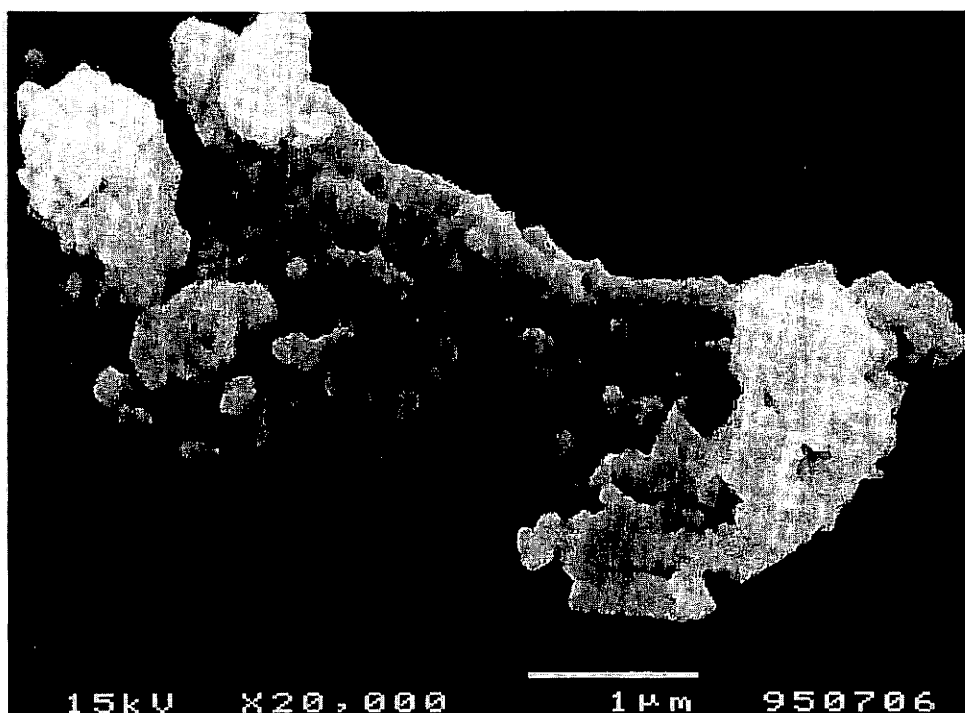


Fig. 5 Scanning electron micrograph and energy dispersive X - ray analysis of the fine particles in the smoke produced by burning polyethylenes. The particle of  $0.1 \mu\text{m}$  in diameter was observed to form an aggregate with others. The major element of the particles is carbon.



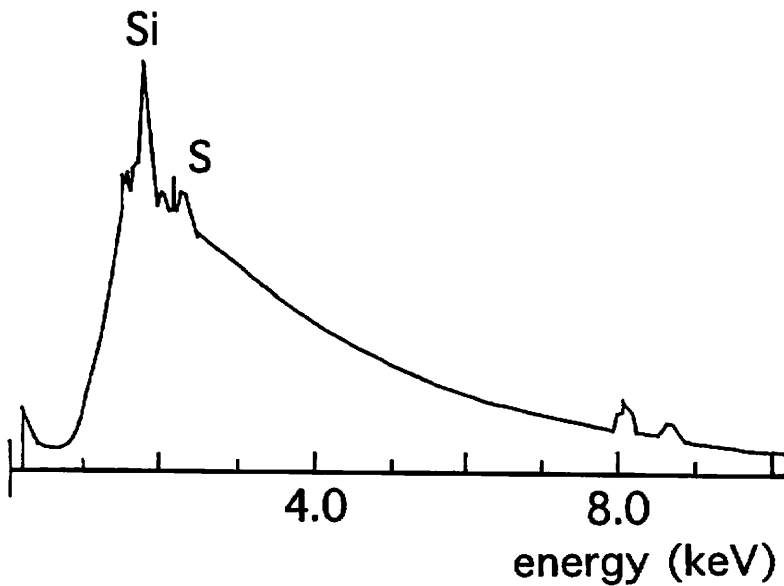
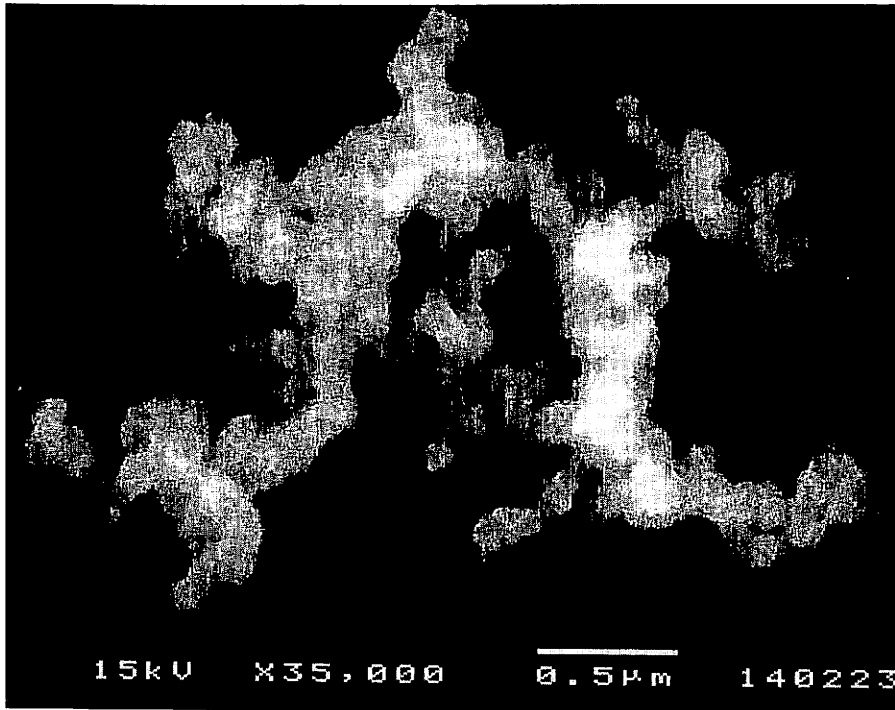


Fig. 6 Scanning electron micrograph and energy dispersive X - ray analysis of the fine particles in the smoke produced by burning newspapers. The particle is about  $0.1 \mu\text{m}$  in diameter, and was observed to be in massive situation. The major element of the particles is carbon.

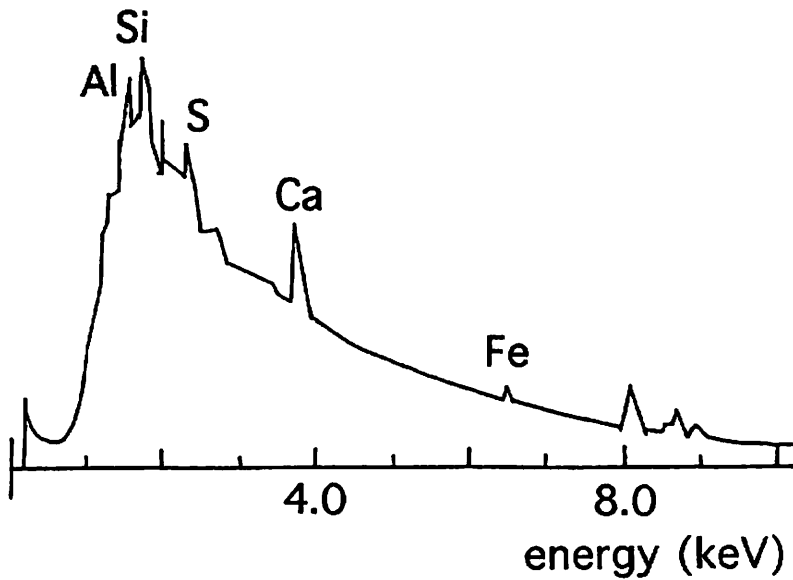
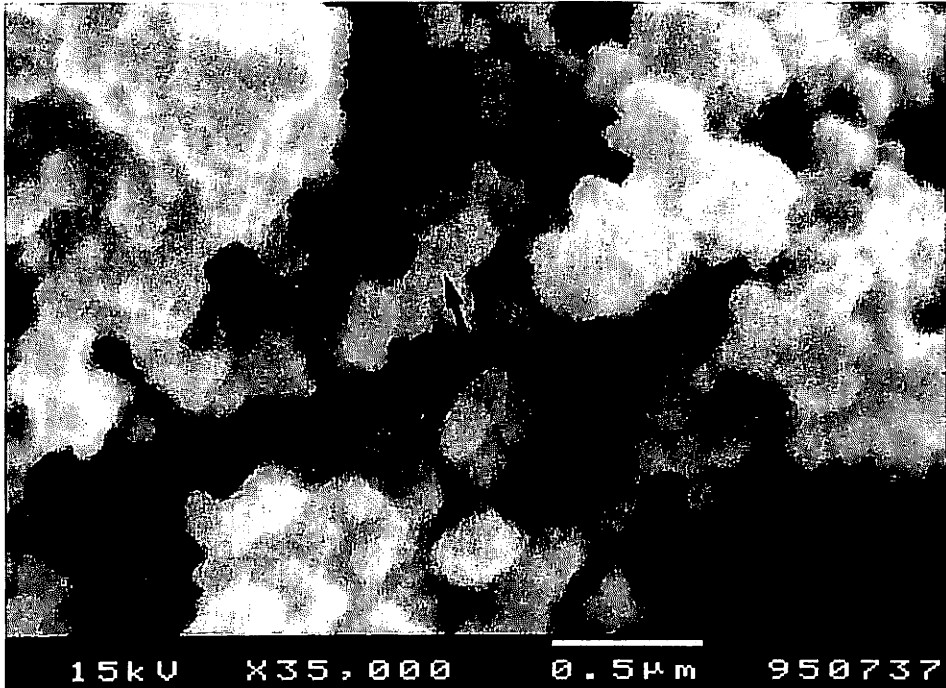


Fig. 7 Scanning electron micrograph and energy dispersive X-ray analysis of the fine particles in the materials obtained from the core of a cassette gas stove. The particle is about  $0.1 \mu\text{m}$  in diameter, and was observed to form an aggregate with others. The major element of the particle is carbon with a small amount of calcium.

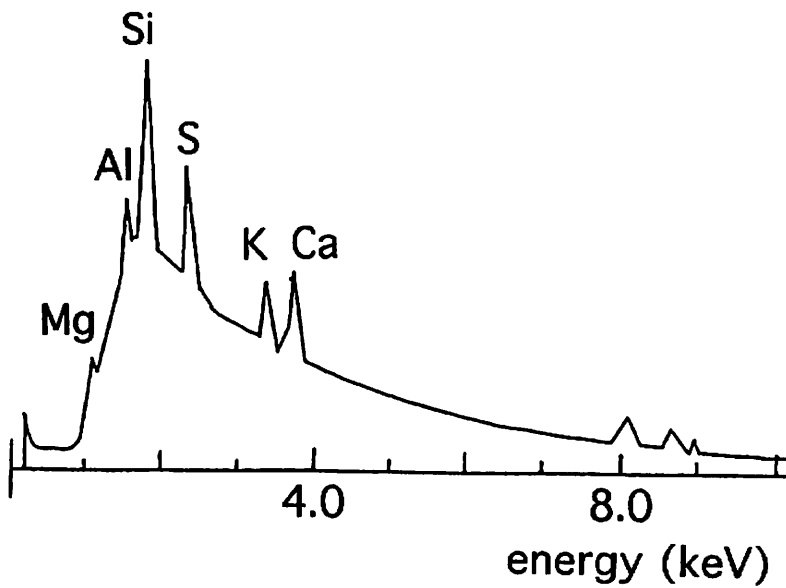
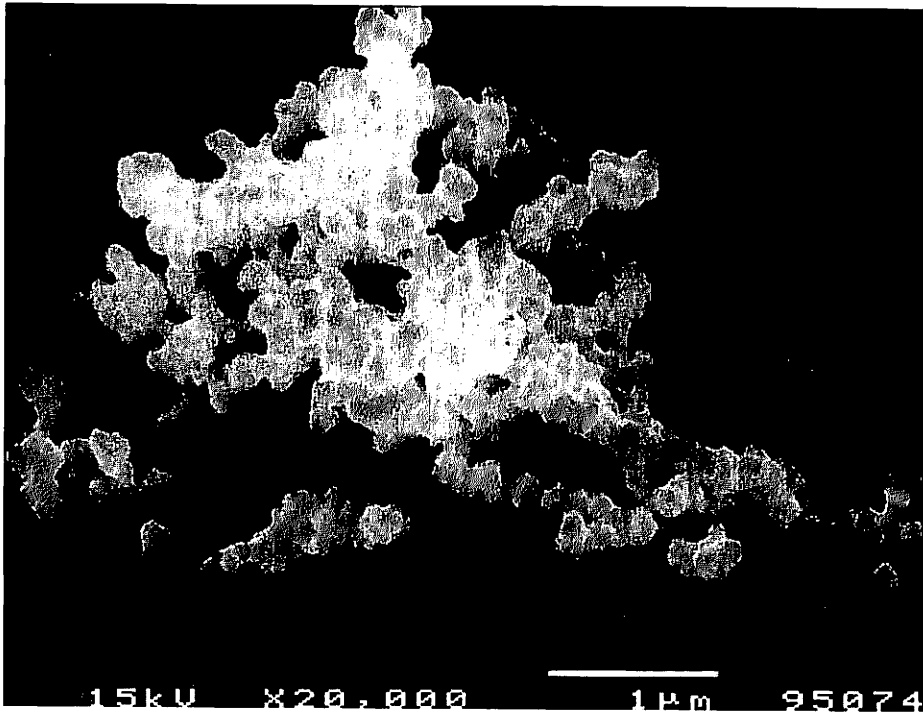


Fig. 8 Scanning electron micrograph and energy dispersive X - ray analysis of the fine particles in the material obtained from the core of an oil heater. The particle is about 0.1  $\mu\text{m}$  in diameter, and was observed to form an aggregate with others. The major element of the particle is carbon with a small amount of silicon, sulfur, potassium and calcium.

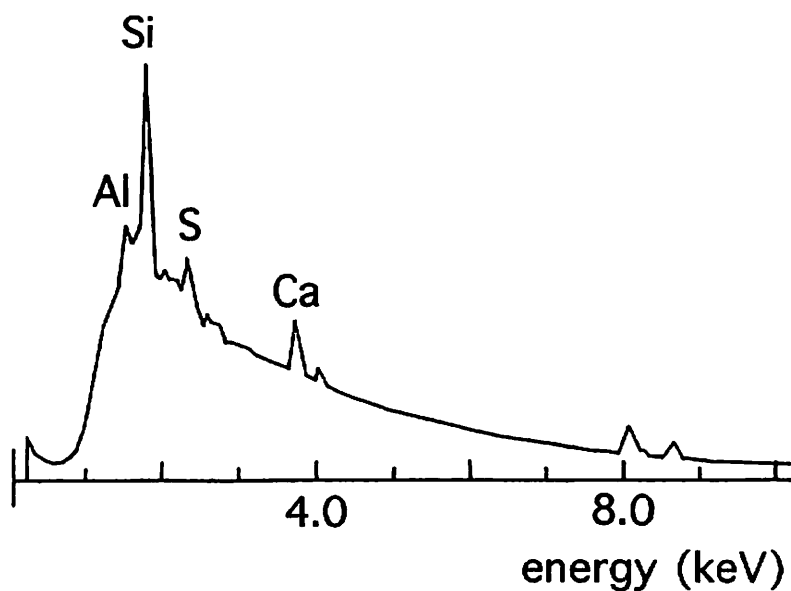
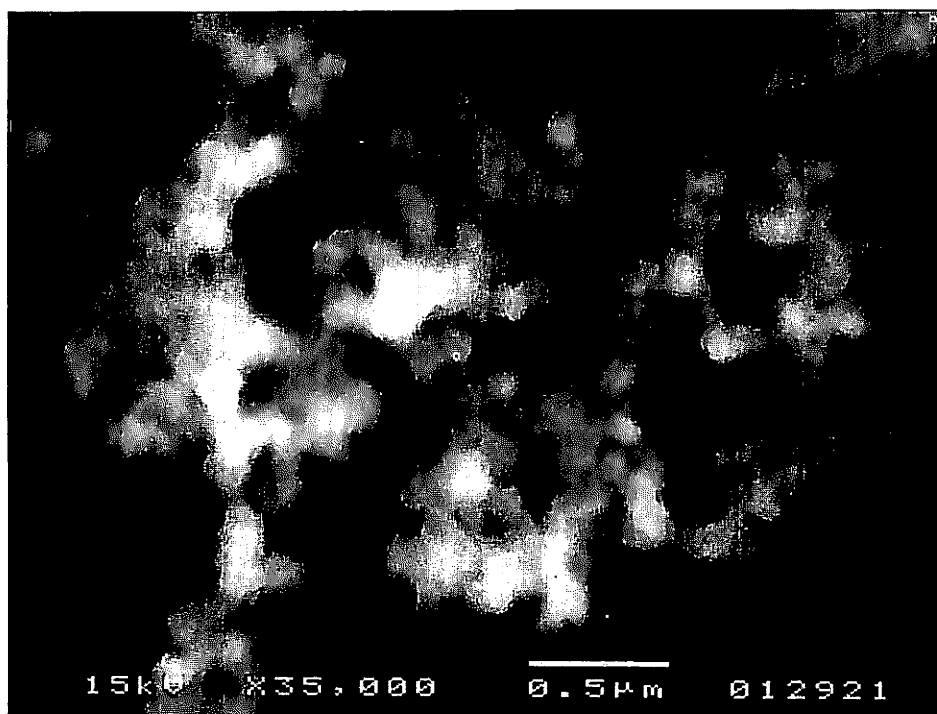


Fig. 9 Scanning electron micrograph and energy dispersive X - ray analysis of the fine particles in the smoke produced by burning coals. The particle is about  $0.1 \mu\text{m}$  in diameter, and was observed to form an aggregate with others. The major element of the particle is carbon with a small amount of silicon, sulfur and calcium.

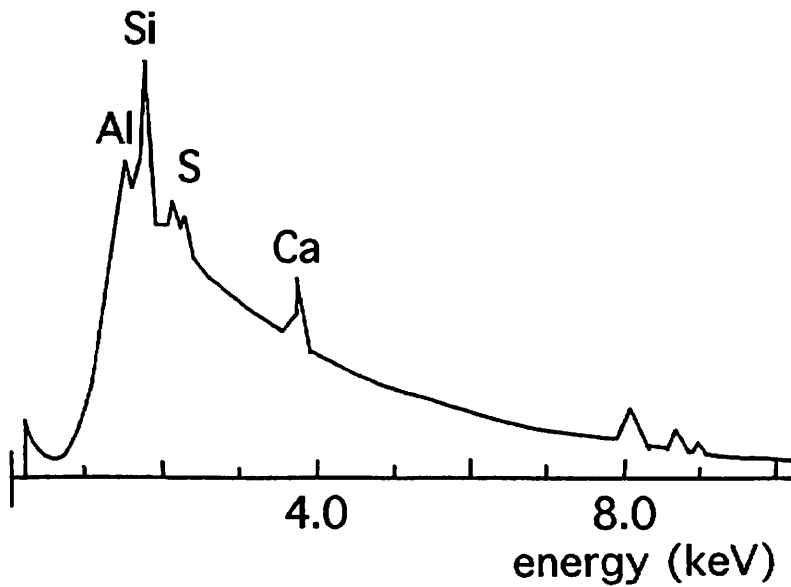
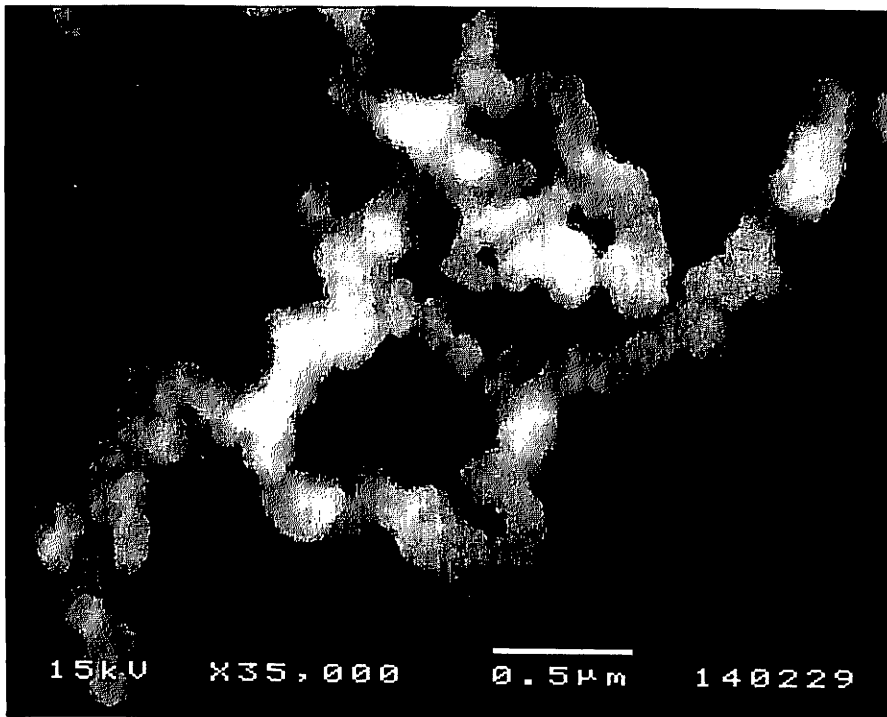


Fig. 10 Scanning electron micrograph and energy dispersive X - ray analysis of the fine particles in the smoke produced by burning polystyrene. The particle is about  $0.1 \mu\text{m}$  in diameter, and was observed to form an aggregate with others. The major element of the particles is carbon with a small amount of silicon, sulfur and calcium.

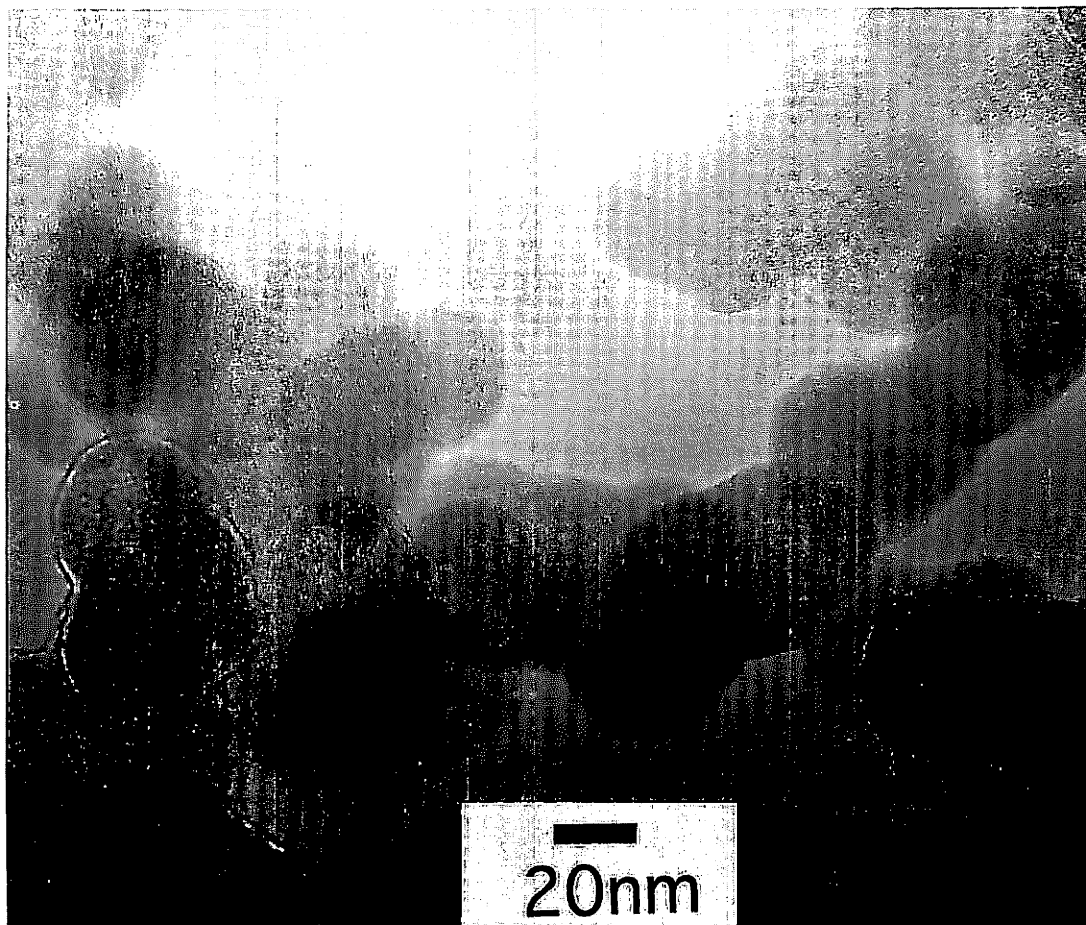


Fig. 11 Transmission electron micrograph of the fine particles in the smoke produced by burning polystyrene. Particles were not isolated, but were identified to be in connecting each others without clear boundaries.

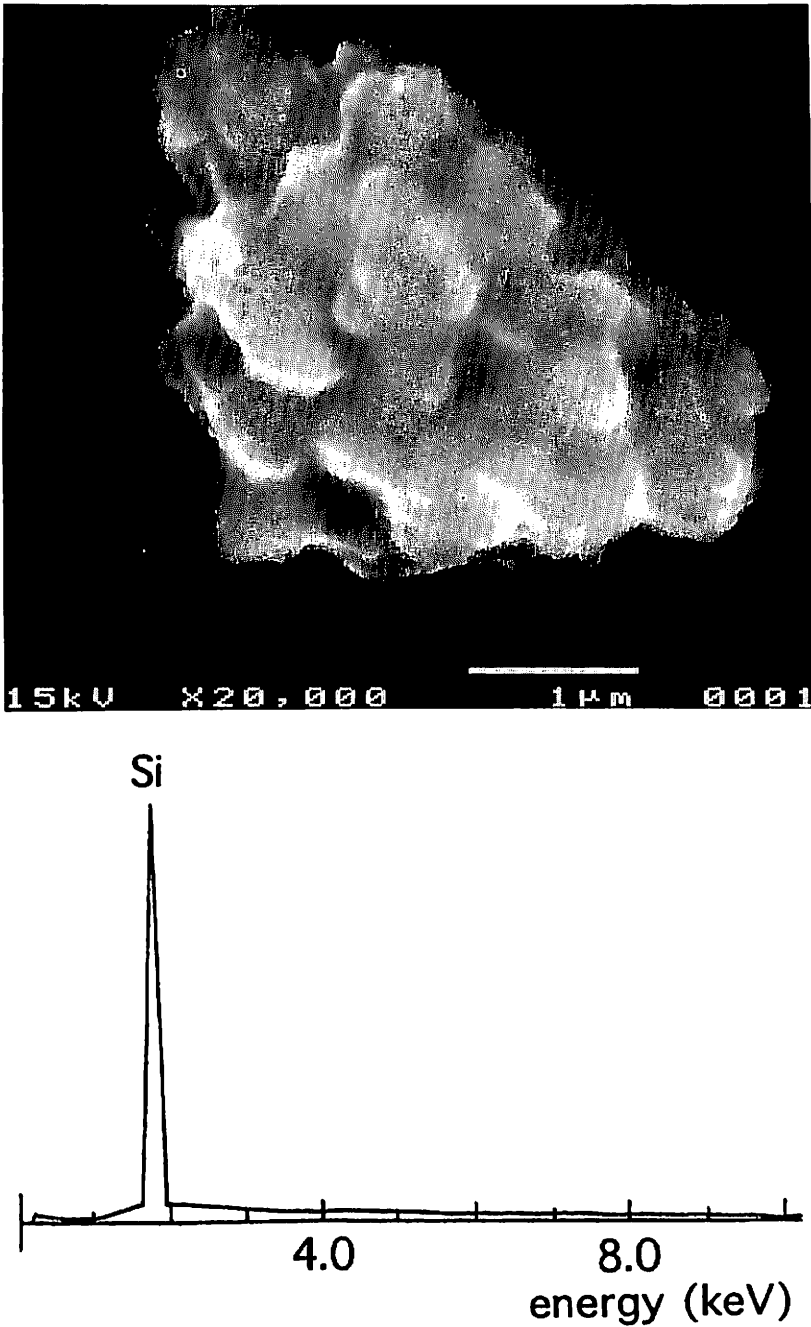


Fig. 12 Scanning electron micrograph and energy dispersive X - ray analysis of the particle in the smoke produced by burning straw. The particle is about  $3 \mu\text{m}$  in diameter, the surface of which was identified to be like "confeito, or konpeito", a Japanese confetti. The element of the particle is pure silicon.

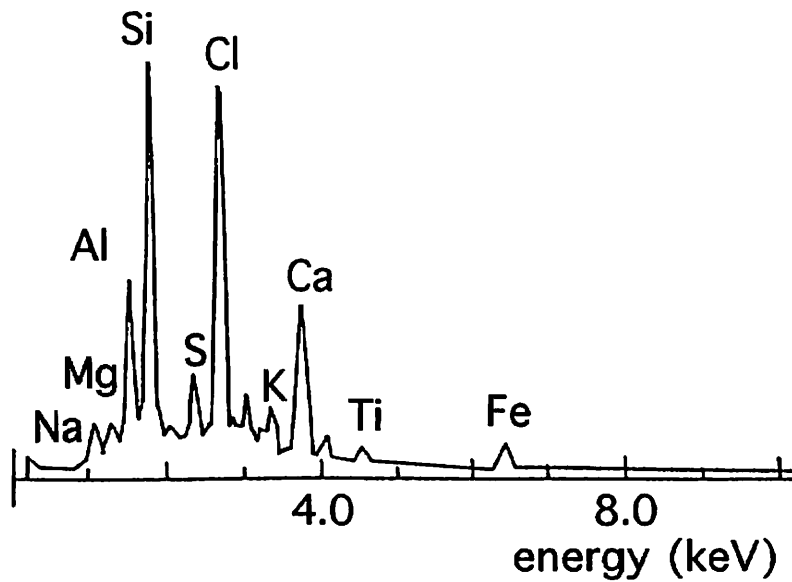
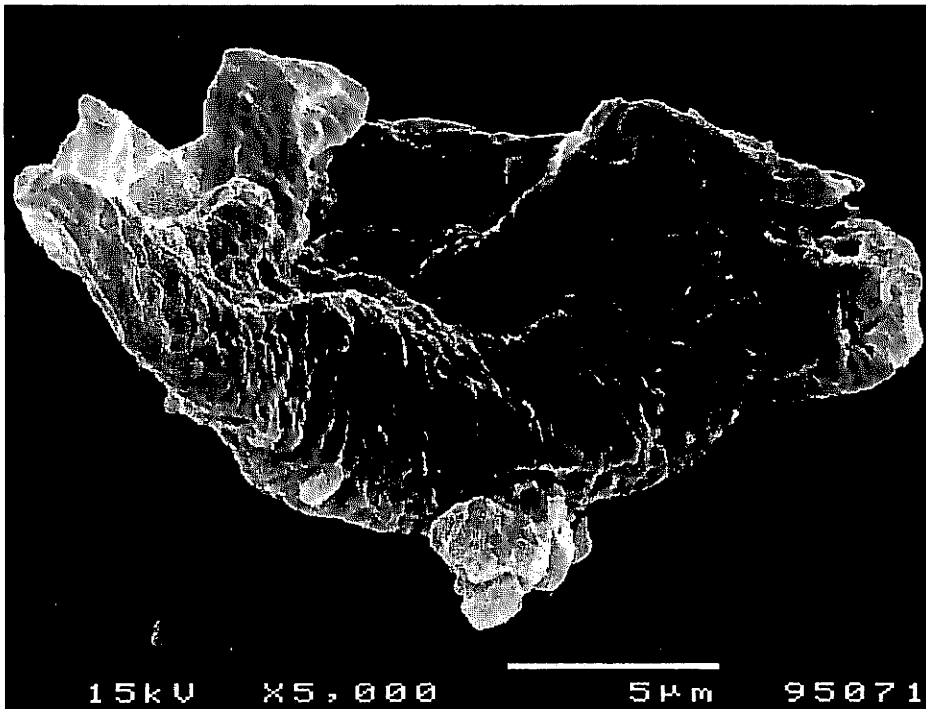


Fig. 13 Scanning electron micrograph and energy dispersive X-ray analysis of the particle in the smoke produced by burning vinyl chlorides. The particle is about  $15\ \mu\text{m}$  in diameter, the form of which looks like a burnt plastic bag. The major elements of the particle are silicon and chlorine, with a small amount of aluminum, sulfur and calcium. Trace elements are sodium, magnesium, potassium, titanium, and iron.



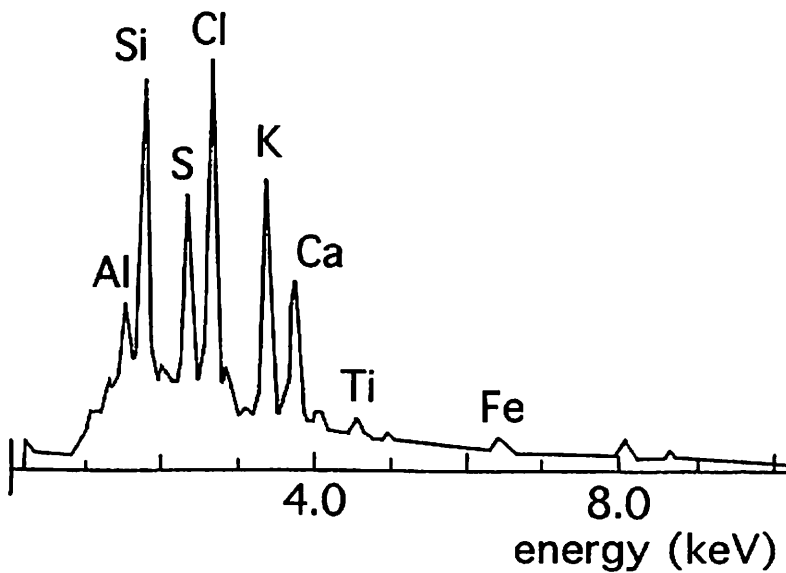
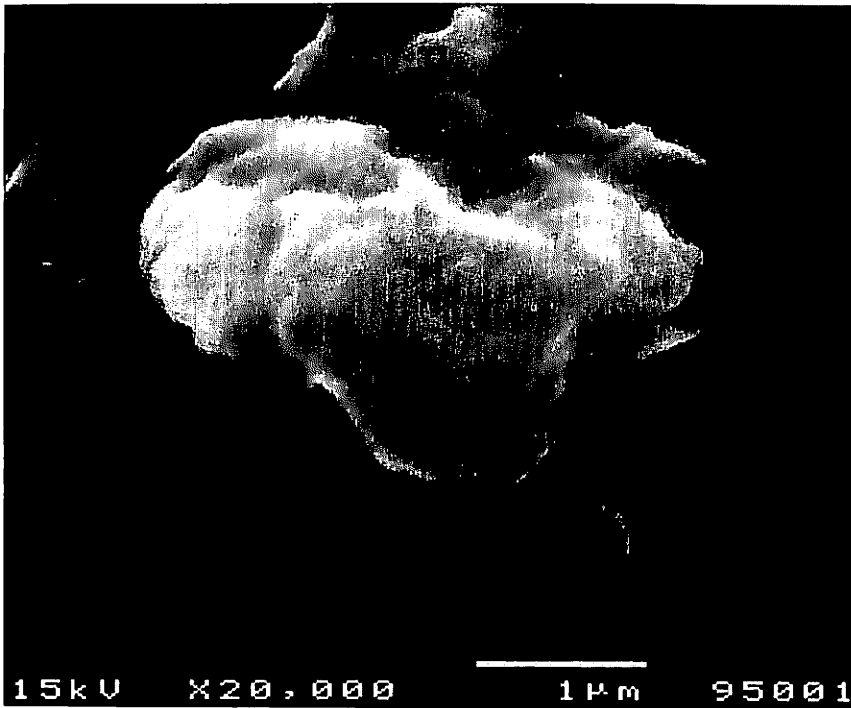


Fig. 14 Scanning electron micrograph and energy dispersive X - ray analysis of the particles in the smoke produced by burning woods. The particle is about  $1 \mu\text{m}$  in diameter, and some of them are stuck each other. The major elements of the particles are silicon, sulfur, chlorine, potassium and calcium with a small amount of aluminum.

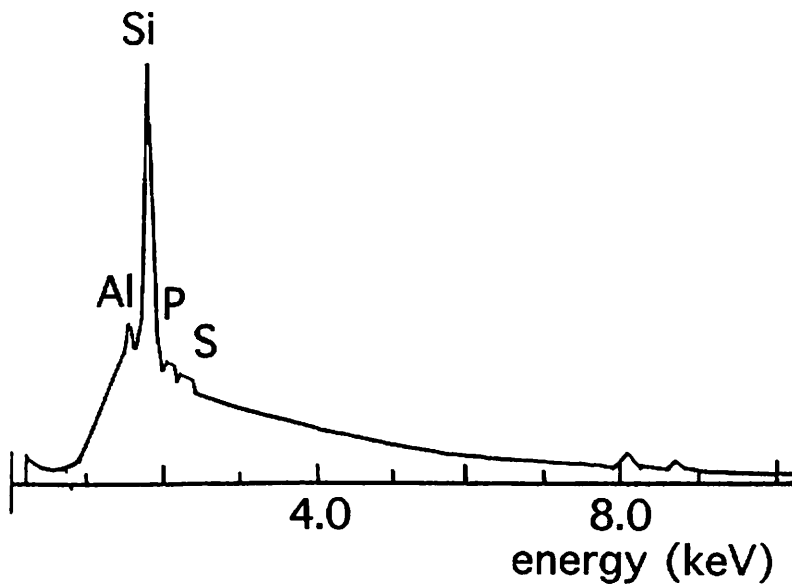
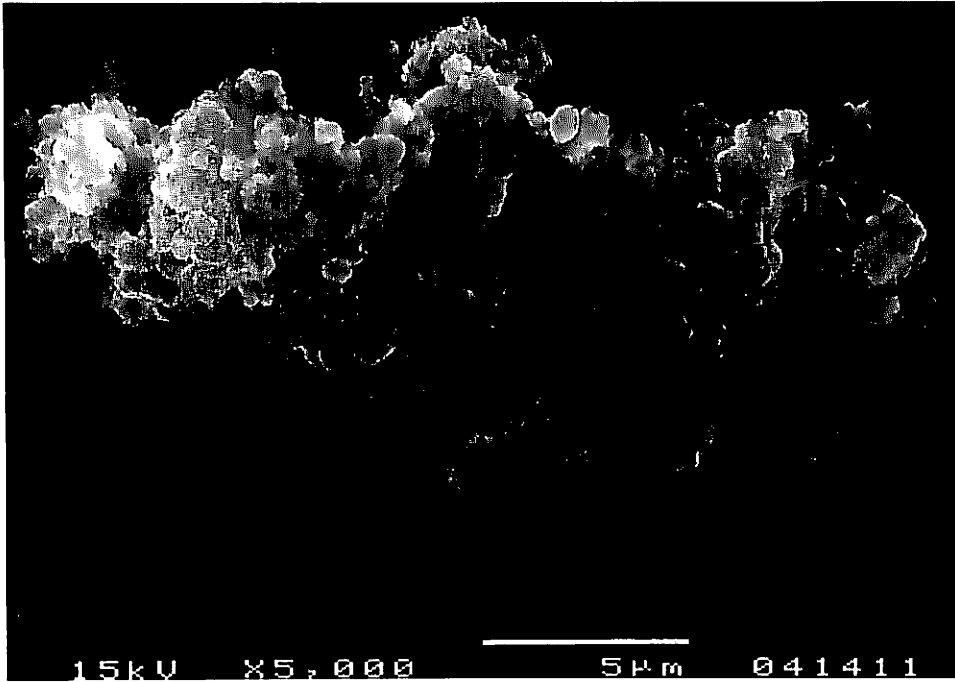


Fig. 15 Scanning electron micrograph and energy dispersive X - ray analysis of the particles in the smoke produced by burning charcoal. The particle is about  $0.5 \mu\text{m}$  in diameter, and was observed to be in aggregative situation. The major element of the particles is silicon with carbon.

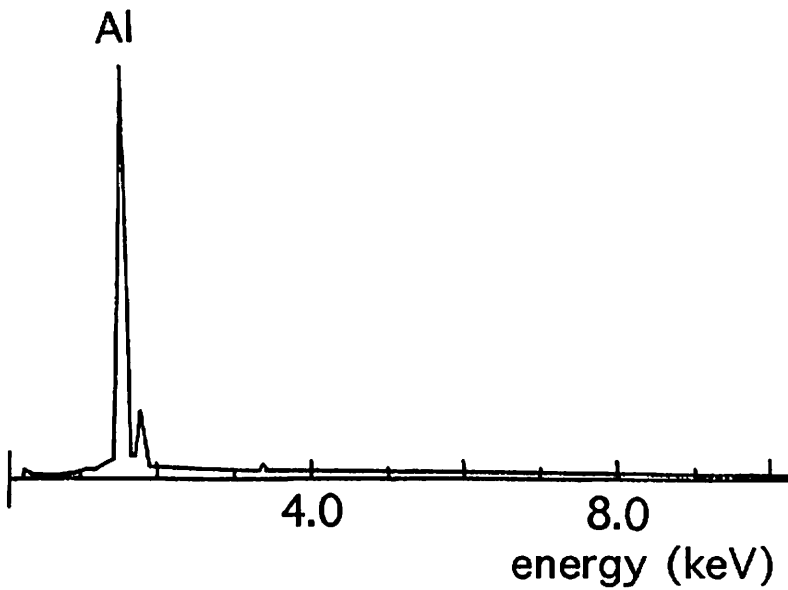
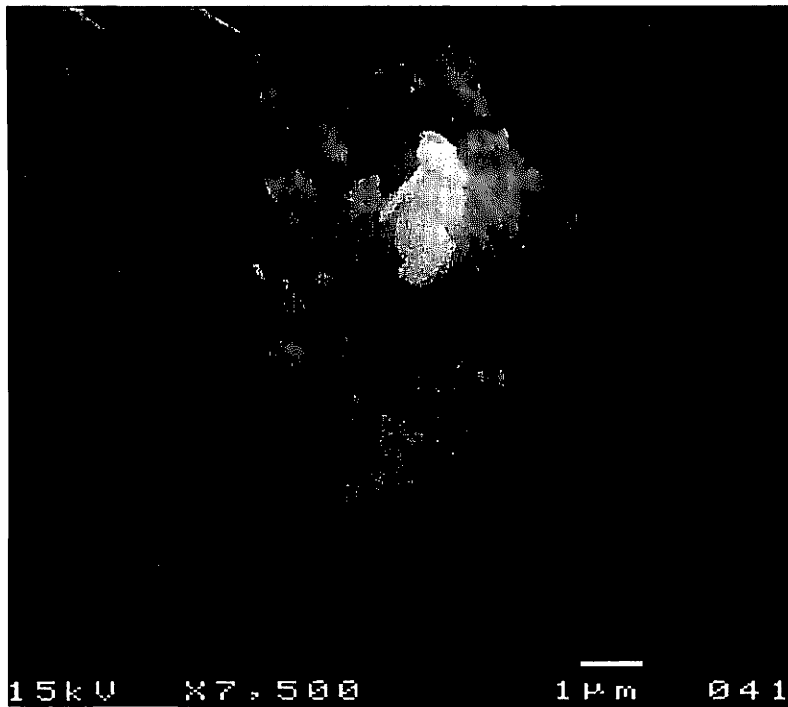


Fig. 16 Scanning electron micrograph and energy dispersive X - ray analysis of the particles in the smoke produced by burning pampas grass. Each particle was observed to be finely fibrous, and compose an aggregate with others. Big-typed particles can be seen in the middle. The major element of the particles is aluminum, and trace element is silicon.

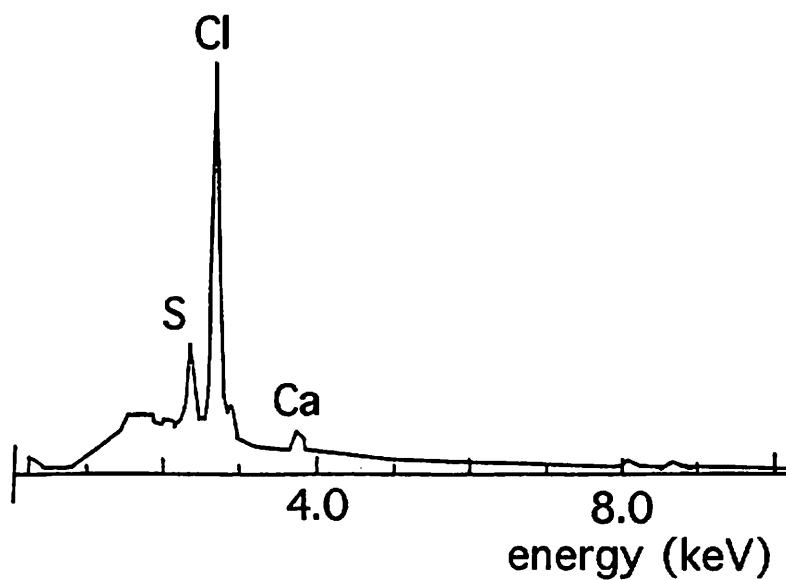
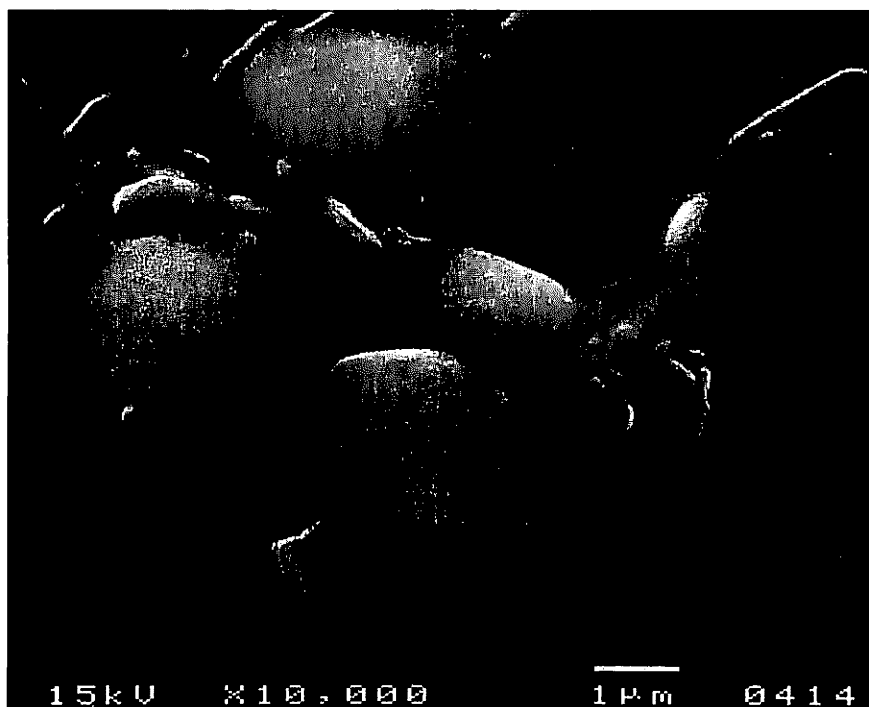


Fig. 17 Scanning electron micrograph and energy dispersive X - ray analysis of the material in the smoke produced by burning pampas grass. Each particle has the featured surface which is coated with a film. The major element of the particles is chlorine.

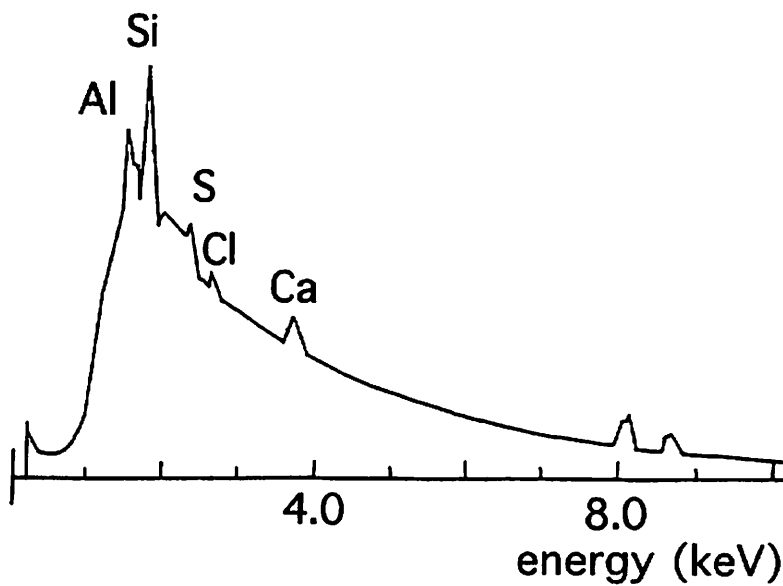
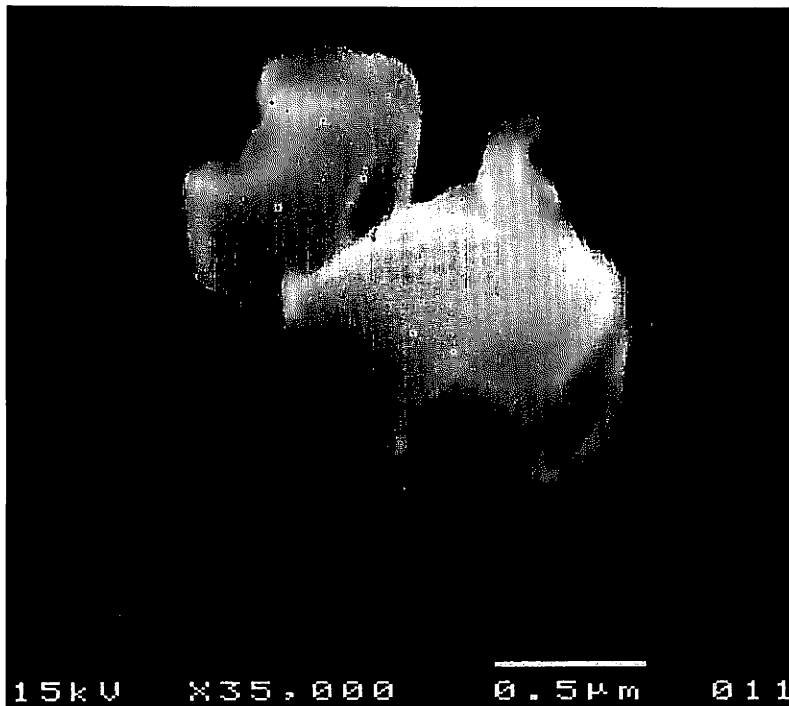


Fig. 18 Scanning electron micrograph and energy dispersive X - ray analysis of the particle in the smoke produced by burning pampas grass. The particle is about  $1 \mu\text{m}$  in diameter, and some particles are stuck each other. Particles were in irregular form respectively. The major element of the particle is carbon with a small amount of silicon.

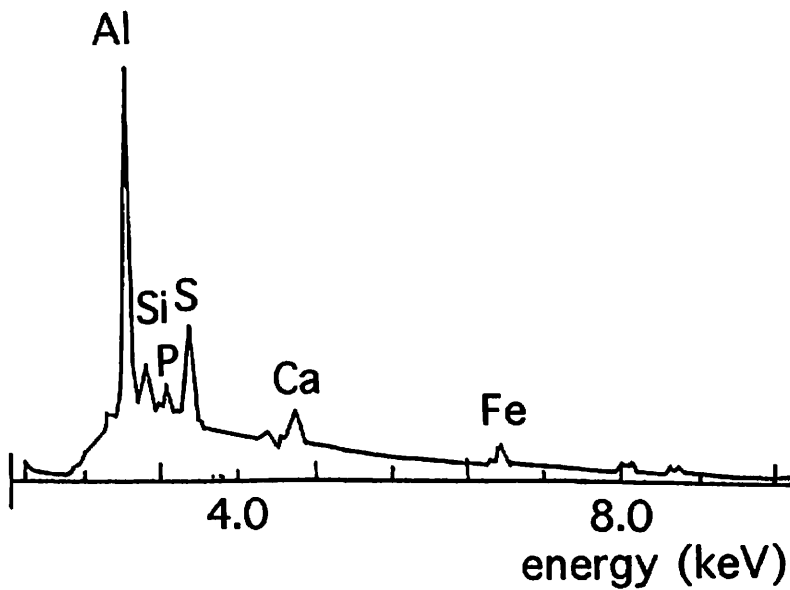
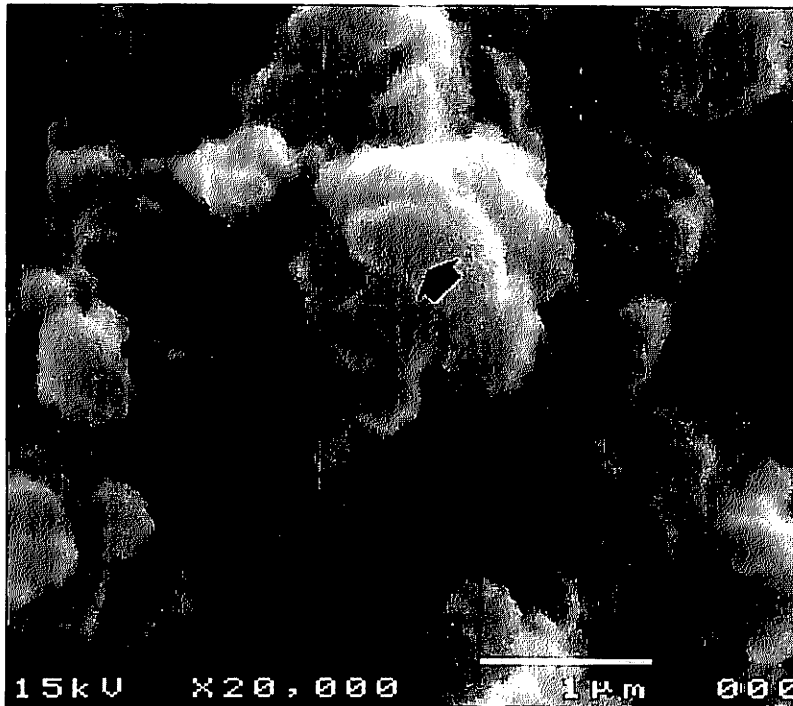


Fig. 19 Scanning electron micrograph and energy dispersive X-ray analysis of the particles in the material collected from the exhaust pipe of a gasoline car. The particle is about  $0.5\sim 2\ \mu\text{m}$  in diameter, and was observed to form an aggregate. The major element of the particle is aluminum with a small amount of silicon, sulfur, calcium and iron.

## 5. Conclusions

Although the samples for observations were produced by the combustion of materials with the work of human hands, as a result of the observations, the particles can be classified into two categories. One is categorized as the particles produced by the combustion of fossil fuel and petrochemical products, such as light oil (diesel) or polyethylenes. The features of the particles involved in this category are spheroidized, 0.1  $\mu\text{m}$  in diameter, and in an aggregative situation. In addition, it was found that such particles were mainly composed of carbon. The other is categorized as the particles produced by the combustion of natural materials, such as woods or straw. The particles involved in this category, comparing to the former, are larger in diameter, and are more various in both size and micromorphology. Such particles were analyzed to be composed of silicon, aluminum and other various elements.

Gasoline is categorized as a fossil fuel. Nevertheless, the observation of the burnt particles of gasoline led to the quite different result, comparing to the ones obtained from the burnt particles of other fossil fuel. The particles were identified to be 1  $\mu\text{m}$  in diameter, and form an aggregate. The major element composing the particles was analyzed to be aluminum.

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