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TRANSMISSION ELECTRON MICROSCOPY IN SOURCE APPORTIONMENT OF AMBIENT AEROSOL

Atmospheric aerosol particles were analyzed by transmission electron microscopy for source identification. The following sources were recognized: crustal sources, power plant emissions, one distant source (a smelter), and secondary sulphate emissions. Some examples of complex-particle histories and reactions were presented.

1. INTRODUCTION

In the past few years, it has become a frequent practice that air pollution authorities use models to develop optimal control strategies for air pollutants. The primary tool of control agencies to determine the contribution of each source to the total level of contamination at sampling sites are source-oriented dispersion models [1-3]. We are aware of the fact that difficulties are sometimes encountered with dispersion models when applied to aerosol data. It is not easy to establish their accuracy, e.g. how close the calculated estimates come to the measured concentrations of total particulate matter.

There are three major factors that account for the trouble mentioned:

1) the considerable contribution of natural sources to the composition of the atmospheric aerosol,

2) the complexity of urban ecosystem, e.g. the concurrent influence of various emissions including fugitive sources,

3) the lack of understanding of the modes by which new particles are formed in the atmosphere, and the complexity of transport of airborne particles.

Item 1) requires additional comments. Thus, the inputs of particulates from natural sources are mostly uncertain, so we usually have trouble with quantifying them. The intensities of these

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sources vary with time and space. However, it is possible to show the significance of natural sources by analyzing wind erosion. At mid-latitudes northern hemisphere the particulate emission from wind erosion is three times as high as the emission from all industrial sources [4].

It is worth noting that future efforts will be directed towards the determination of the portion of inhalable and fine-particle size, as well as the sources of particulates in certain size ranges. Unfortunately, dispersion models fail to give such information. Having these all in mind, it becomes obvious that other models must be taken into account in air pollution control.

Some recent developments in sampling [5], [6] and analytical methods for particles[7], [8] offer significant support for the utility of receptor models. Receptor models involve observations at sampling sites, the receptors, and aim at assessing the contributions of various sources.

Receptor models may be grouped into two basic categories – particulate source apportionment models and models dealing with exposure commitment assessment. The category of particulate source apportionment models subdivides to describe microscopic and mathematical methods.

This paper is a part of intensive study on receptor models. It makes use of transmission electron microscopy (TEM) and X-ray diffractometry (XRD) for quantitative analysis of particles and for source apportionment of ambient aerosol.

2. EXPERIMENTAL

Sampling was carried out with a high-volume air sampler 12 km from a lignite-fired power plant. Aerosol samples were collected direct onto TESLA BS-540 TEM grids containing holey-carbon support films. The grids were mounted on glass fibre filters (of TFA-810 type) placed within sampling devices. Good deposits for TEM analysis were collected in 20 min.

3. RESULTS AND DISCUSSION

Figures 1 and 2 give typical aerosol particles collected at the investigated sampling sites. As shown by these micrographs, particle size varies within a wide range. Despite the distinct occurrence of large grain size, the number concentration of aerosol particles with diameter smaller then 1 μm is dominated. A close examination of large grain size (greater than 3 μm) has revealed that large particles owe their origin to non-burnt coal and coke, as well as to sharp-edged crustal matter. Identified were particles of kaolinite, calcite, quartz, microcline, and muscovite. Single crystals are shown in figs. 3 and 4 for the purpose of illustration. The presence of the particles listed above offers a good support for the contribution of crustal sources to the composition of the aerosol. Micrographs 5, 6 and 7 give a number of typical agglomerates which probably form during sample deposition on the TEM grid. Among the various particles, we

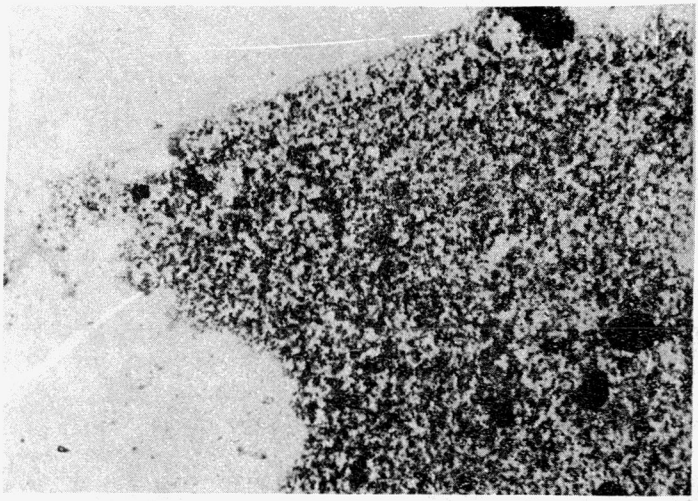

Fig. 1. Typical aerosol particles collected near the power plant (1 cm =2.9 μm)
Rys. 1. Typowe cząsteczki aerozolu pobrane w pobliżu elektrowni (1 cm = 2,9 μm)

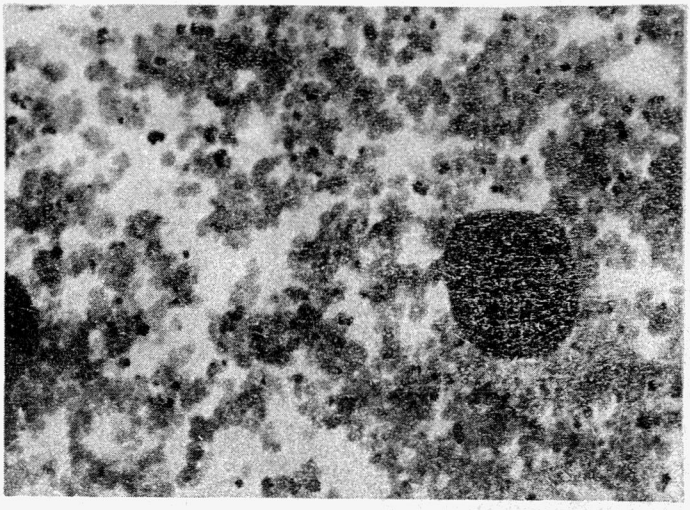

Fig. 2. Typical aerosol particles collected near the power plant (1 cm = 0.4 μm)
Rys. 2. Typowe cząsteczki aerozolu pobrane w pobliżu elektrowni (1 cm = 0,4 μm)

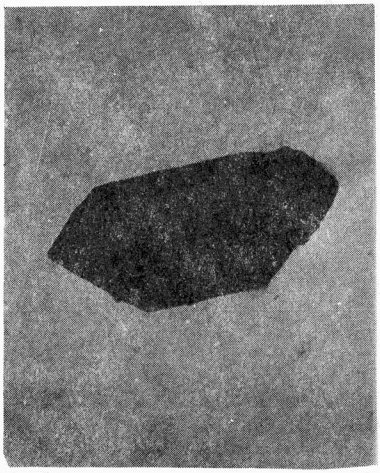

Fig. 3. Single crystal of kaolinite (1 cm = 0.4 μm)
Rys. 3. Pojedynczy kryształ kaolinitu
(1 cm = 0,4 μm)

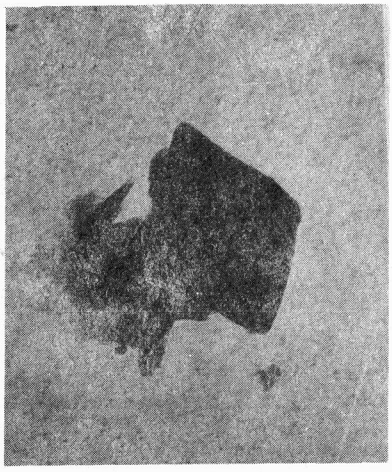

Fig. 4. Single crystal of calcite (1 cm = 0.4 μm)
Rys. 4. Pojedynczy kryształ kalcytu
(1 cm = 0,4 μm)

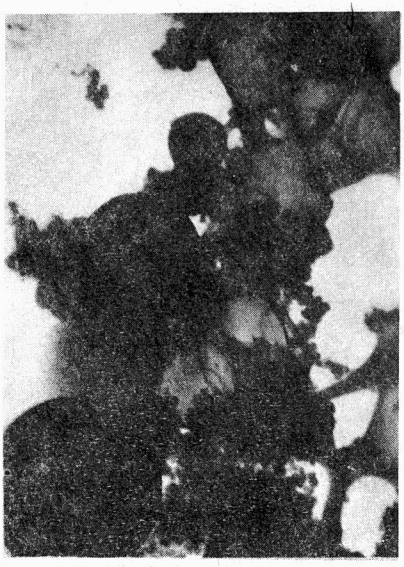

Fig. 5. Some soot/fly ash-type particles
(1 cm = 0.8 μm)
Rys. 5. Niektóre cząsteczki typu sadza/lotny popiół (1 cm = 0,8 μm)

may distinguish the circular shape of 0.5 μm to 3 μm diameter fly ash grains, magnetite spheres of a similar size, and carbon black. All of these constitute a typical feature of particulate emissions from a coal-fired power plant. Analysis of aerosol samples has also revealed the presence of some unusual and fascinating particles (figs. 8, 9, 10). Figure 8 shows clusters of very fine spheres (< 0.15 μm). In figs. 9 and 10, similar spheres are connected to each other with fibres of carbon. Typical filamentous carbon particles found in aerosol samples are associated with high-temperature processes. They are produced in petrochemical industries and smelters [9],[10]. Although the application of the XRD method failed to identify these fine spheres, they are likely to be metal particles, e.g. alloys. Such information may be found in the literature [9]–[11]. The formation of those particles occurs by the build-up of carbon generated by catalytic

Fig. 6. Some soot/fly ash-type particles (1 cm = 0.8 μm)
Rys. 6. Niektóre cząsteczki typu sadza/lotny popiół (1 cm = 0,8 μm)

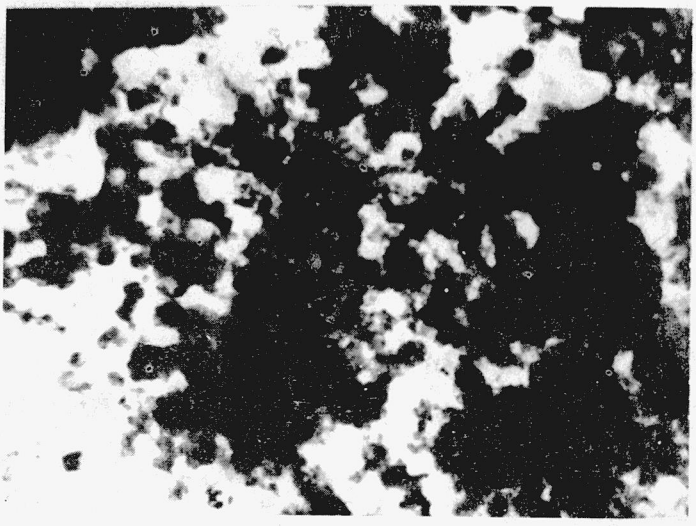

Fig. 7. Typical soot particle (1 cm = 0.8 μm)
Rys. 7. Typowe cząsteczki sadzy (1 cm =0,8 μm)

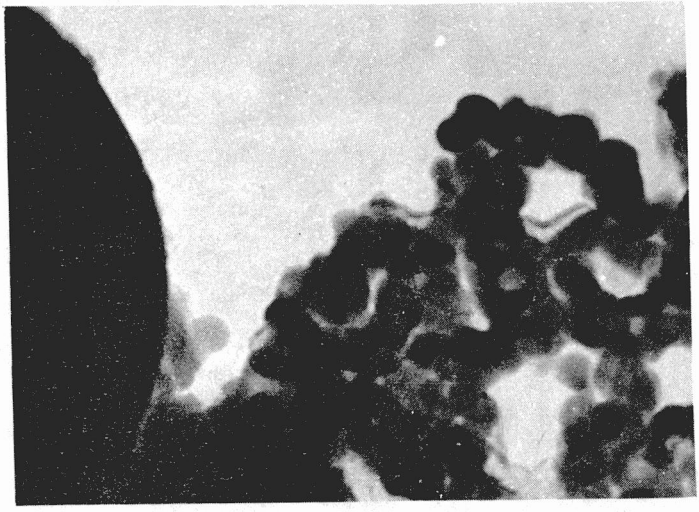

Fig. 8. Cluster of very fine spheres (1 cm = 0.15 μm)
Rys. 8. Aglomeraty bardzo drobnych kulek (1 cm = 0,15 μm)

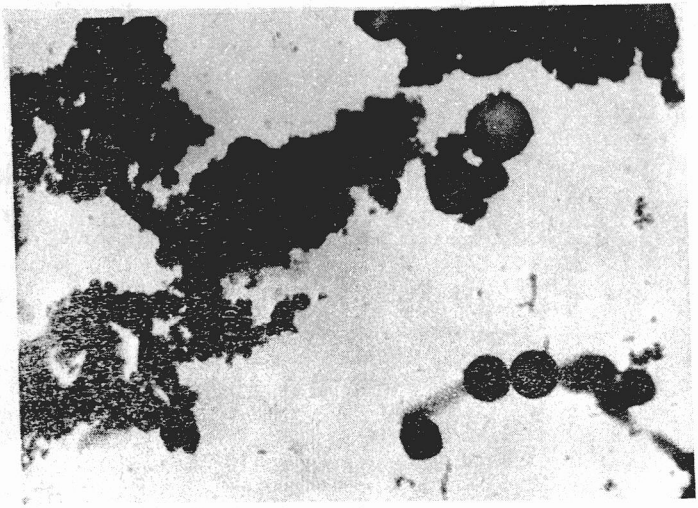

Fig. 9. Filamentous carbon cluster (1 cm = 2.9 μm)
Rys. 9. Włókniste cząsteczki węgla (1 cm = 2,9 μm)

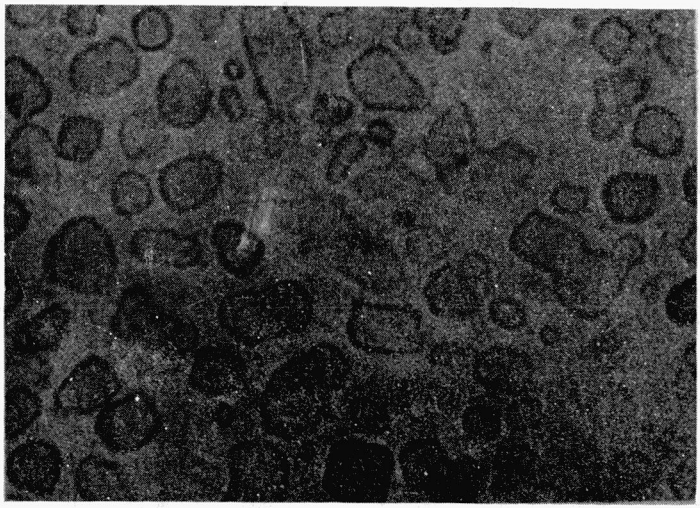

Fig. 10. Filamentous carbon cluster (1 cm = 0.4 μm)
Rys. 10. Włókniste cząsteczki węgla (1 cm = 0,4 μm)

Fig. 11. Fine crystals of ammonium sulphate (1 cm = 0.067 μm)
Rys. 11. Drobne kryształy siarczanu amonowego (1 cm = 0,067 μm)

decomposition of carbon-bearing gases on one side of the metal particle. Thus, Cu–Zn alloys are associated with smelters as the contributing sources.

High concentrations of copper and zinc measured during south and south-westerly advection of air masses, on one hand, and the strong correlation between these two metals, on the other hand, indicate the same origin of copper and zinc particles. The particles in question are likely to be associated with long-range transport (a smelter is situated about 50 km from the sampling sites).

Another example of an individual airborne particle type, that provides information both about the source apportionment and about the reactions determining its formation, are the particles of micrograph 11. Fine crystals surrounding the particles or their agglomerates over large areas are ammonium sulphates. They fail to form agglomerates because their competition for water vapour particles has an unfavourable influence on both coalescence and growth. The presence of many very fine particles of 0.05 μm diameter or less (nucleation mode) may indicate the production of new particles in the atmosphere. Figure 12 shows some characteristic particles. Among them sulphuric acid and partly neutralized sulphate particles have been identified. They exhibit a distinctive morphology which is observed by TEM.

Sulphuric acid or partly neutralized sulphate appear as single spherical caps surrounded by one or more rings of smaller particles [12], [13].

4. CONCLUSIONS

Application of the TEM method has revealed that it is possible to examine individual particles and obtain detailed information (chemical and physical) which might ultimately lead to an understanding of the origin of the particles and the reactions which determine their formation. In this study four sources, which might influence the composition of the aerosol at the sampling sites under investigation, were pinpointed. These are as follows: crustal sources, power plant emissions, one distant source (probably a smelter), and secondary sulphate emission. It is interesting to note that sorce determination depends upon detailed characterization of particles emitted from known or suspected sources. Hence, there is a need of making an atlas of micrographs and typical electron diffractions for individual particle types which owe their origin to many different emission sources. It is obvious that these will be of considerable help in recognizing the sources of many fine particles which occur in the atmosphere.

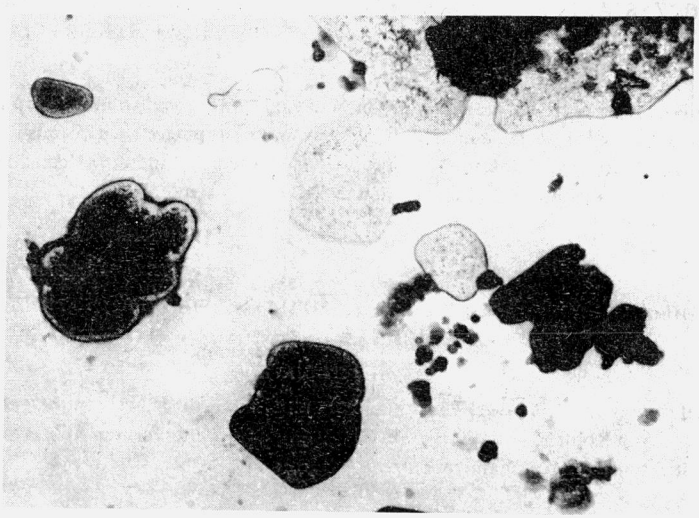

Fig. 12. Examples of particles coated with a layer of acid or sulphates (1 cm = 0.4 μm)
Rys. 12. Przykłady cząsteczek pokrytych warstwą kwasu lub siarczanów (1 cm = 0,4 μm)

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WYKORZYSTANIE TRANSMISYJNEGO MIKROSKOPU ELEKTRONOWEGO DO IDENTYFIKACJI ŹRÓDEŁ POCHODZENIA AEROZOLU ATMOSFERYCZNEGO

Próbki aerozolu atmosferycznego analizowano przy użyciu transmisyjnego mikroskopu elektronowego w celu rozpoznania ich źródeł pochodzenia. Zidentyfikowano następujące źródła emisji: źródła krustalne, elektrownię węglową, hutę metali kolorowych oraz wtórną emisję siarczanów. Pokazano kilka przykładów złożonej historii powstawania mikrocząstek oraz ich reakcji w atmosferze.

DIE ANWENDUNG VON ELEKTRONMIKROSKOPIE ZUR BESTIMMUNG DER QUELLEN DES AROSOLS

Arosolpartikel werden mit Hilfe des Elektronmikroskops untersucht. Es werden folgende Quellen identifiziert: Emissionen vom Kohlenelektrizitatswerk, Emissionen von weitenfernter Kupferhutte, Sulfatemission und Staub von Strassen- und Autobahnverkehr.

ПРИМЕНЕНИЕ ТРАНСМИССИОННОГО ЭЛЕКТРОННОГО МИКРОСКОПА ДЛЯ ИДЕНТИФИКАЦИИ ИСТОЧНИКОВ ПРОИСХОЖДЕНИЯ АТМОСФЕРНОГО АЭРОЗОЛЯ

Пробы атмосферного аэрозоля анализировались с помощью трансмиссионного электронного микроскопа в целях распознания источников их происхождения. Были идентифицированы следующие источники эмиссии: естественные источники, угольная электростанция, плавильный завод цветных металлов, а также вторичная эмиссия сульфатов. Показано несколько примеров сложной истории образования микрочастиц и их реакции в атмосфере.