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## IDENTIFICATION OF COAL FLY-ASH PARTICLES IN AMBIENT AEROSOLS

Microscopic and diffraction methods are often inadequately appreciated when investigating aerosols and fly-ash. In this study these methods are used for the investigation of fly-ash samples (collected within area of a lignite-fired power plant), as well as aerosols samples (taken 4 km from the emitter, and in the recreation area 1362 m a.s.l.). Each sample contained aluminosilicates, quartz and iron compounds. Identification of ammonium sulphate in aerosol enables analysis of transformation and long-range transport of air pollutants. The size and shape of  $> 0.1 \mu\text{m}$  particles were determined using transmission electron microscopy, electron diffraction being applied for structure investigation. Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy was used to determine the size, shape, surface and elemental composition of  $> 1 \mu\text{m}$  particles. Mineralogical composition of fly-ash was established using X-ray diffraction. The results substantiate the utility of microscopic and diffraction methods in aerosol investigation and source apportionment.

### 1. INTRODUCTION

Industrial fine particles ( $< 2 \mu\text{m}$  in diameter) have health implication to man because of high concentrations of toxic substances accumulating on the available surface area. These are organic tars, heavy metals, and radioactive elements (LODGE [10], LANNEFORS and HANSSON [9], SHOW and PAUR [13], SPENGLER and THURSTON [15], ZWOŹDZIAK [16]). Fine particles have their contribution to such phenomena as visible degradation, acid precipitation, and long-range transport of air pollutants (RODHE et al. [11], JOHNSON and SICCAMI [8], SHAH et al. [12]). Airborne particles are often vapour condensation nuclei and centres of gas adsorption in the atmosphere.

Future air quality standards will probably require knowledge of concentration

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and chemical composition of fine aerosol. The presence of some of the elements or chemical compounds in the atmospheric aerosol clearly indicates the source of their origin. Assuming, furthermore, that particles emitted from a specific source display characteristic morphology, structure and chemical composition, it is possible to determine the source of atmospheric particles on the basis of their identification. Although a variety of methods and, also, equipment are now in use for the examination of particulate matter in general, they are rarely applied to airborne particle study, if at all (HOCK and LICHTMAN [6], BENOYER et al. [2], HOPPE and PATZEIT [7]).

This paper presents the possible applications of microscopic and diffraction methods to identify not only particles from coal-fired power plants, but aerosol particles as well. In this study the following procedures were involved:

transmission electron microscopy (TEM) to determine the size and shape of  $> 0.1 \mu\text{m}$  particles as well as their structure, using selected area electron diffraction (SAED),

scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDXS) to determine the size, shape, surface and chemical composition of  $> 1 \mu\text{m}$  particles,

X-ray diffraction (XRD) to examine the mineralogical composition.

## 2. METHODS

Samples of fly-ash emitted from a lignite-fired power plant (referred to as plant T) and samples of aerosol particles were collected in two sites. One of these was located approximately 4 km from plant T, and other at the summit of Szrenica (1362 m a.s.l.). The samples of aerosol particles were taken at wind direction from plant T.

At the initial stage of the study, aerosol samples for EM analyses were collected on paper and membrane filters. Then, they were separated in the sonic generator and settled onto copper grids containing holey-carbon support films. But this method was soon abandoned, because the preparation procedure was too complicated and the representativeness was very poor. Copper grids were mounted direct onto filters. However, the best results were obtained when aerosol samples were collected direct onto the copper grids which had been placed in a microvessel of special design, the "Receptor" (fig. 1). The microvessel was joined to a membrane pump (with a delivery of  $80 \text{ dm}^3/\text{h}$ ). Exposure times were adjusted (by experiments) to particles concentration and air humidity at the sampling site.

Because of the considerable amount of coarse fraction present in coal fly-ash samples, particles were separated by sedimentation. Following completion of the process, the portion of particles that remained in suspension was settled onto copper grids containing holey-carbon support (for EM analyses) and onto glass plates (for diffraction analyses).

The following apparatuses were used in this study:

1. Transmission electron microscope Tesla BS-540, with accelerating voltage of 120 kV and microscope constant  $2\lambda L \approx 35 \text{ \AA} \times \text{mm}$ ; during analysis the preparation holder was cooled with liquid nitrogen.

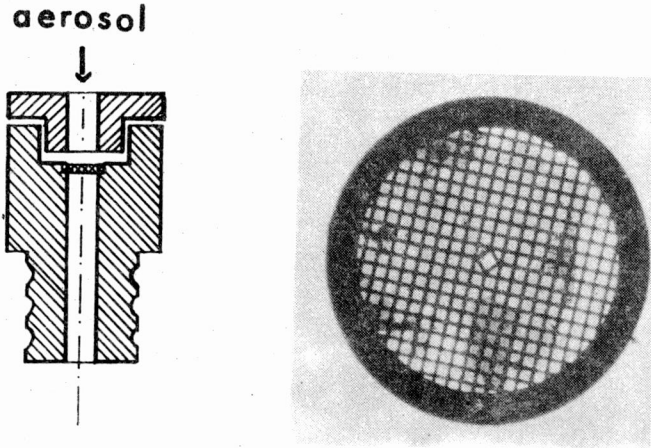


Fig. 1. "Receptor" microvessel and copper grid

2. Scanning electron microscope Stereoscan 180 Cambridge Instruments, with accelerating voltage of 20 kV and electron beam intensity of  $10^{-10} \text{ A}$ .

3. Vacuum coating plant HBA Zeiss to coat grids with holey-carbon films, and vacuum evaporator E306 Edwards to coat specimens with carbon (thus providing electron conduction).

4. X-ray diffraction HZG-4 (made in GDR).

5. Interface Link System equipped with semiconducting X-ray detector for X-ray microanalyses; elemental analyses were carried out in point, and the results were recorded in the form of characteristic X-radiation spectra of elements present in the specimen.

### 3. RESULTS

XRD analyses have revealed aluminosilicates and quartz as the major constituents of fly-ash from plant T (table). SEM and TEM analyses made it possible to distinguish three characteristic groups of particles:

- 1) spherical ( $< 3 \mu\text{m}$  in diameter) (figs. 2a, 2b),
- 2) irregular thin flakes (ca  $3 \mu\text{m}$  in equivalent diameter) (figs. 3a, 3b),
- 3) irregular particles of iron compounds (ca 2 to  $20 \mu\text{m}$  in equivalent diameter) (figs. 4a, 4b).

Studies on the chemical composition (EDXS) have shown that spherical particles are aluminosilicates with such impurities as K, Ca, Fe. The presence of Cu should be

X-ray diffraction pattern of fly-ash emitted by plant T

Angular position of reflection $2\theta$	Relative intensity of lines $I_{rel}$	Interplanar distance determined in fly-ash $d$ [nm]	Interplanar distance for substances identified in powder diffraction file $d$ [nm]			
			$\text{SiO}_2$	$\text{Al}_6\text{Si}_2\text{O}_{15}$	$\text{Al}_2\text{SiO}_5$	$\text{Al}_2\text{SiO}_5$
16.5	15	5.37		5.39	5.35	5.36
20.95	15	4.24	4.26			
25.5	10	3.49		3.43		3.47
26.2	20	3.40		3.39	3.41	3.37
26.7	100	3.34	3.34		3.36	
31.1	10	2.88			2.88	
33.3	20	2.69		2.69	2.67	2.68
35.35	15	2.54		2.54	2.53	2.54
35.8	10	2.51				
36.6	15	2.46	2.46			
37.2	5	2.42				
37.8	5	2.38				
39.5	10	2.28	2.28			
40.9	20	2.21		2.21	2.20	2.20
42.6	10	2.12	2.13	2.12		2.11
45.9	5	1.98				
49.6	5	1.84				
50.3	5	1.81	1.82			
54.2	5	1.69				
57.6	10	1.60				
58.35	5	1.58				
60.2	10	1.54	1.54			
60.8	15	1.52		1.52	1.52	1.52
61.65	10	1.50				

attributed to background radiation (copper grid) (fig.2c). Similar studies on fine flake particles, confirmed by EDXS, have revealed quartz as the constituent of these particles (fig. 3c). The very fine particles (investigated by SAED) are found to be amorphous. Spongy structures, cenospheres and plerospheres are characteristic forms of particles from coal combustion. But none of these were present in fine fraction (CHENG et al. [1], FISCHER et al. [5]). Hence, these particles are associated with coarse fractions. And this can be explained by the mechanism of fly-ash generation. Cenospheres and plerospheres owe their origin to intensive gas release. Gas release is the result of the rapid increase in charge temperature (FISHER et al. [4]). SMITH et al. [14] showed that some of the large particles burst during gas

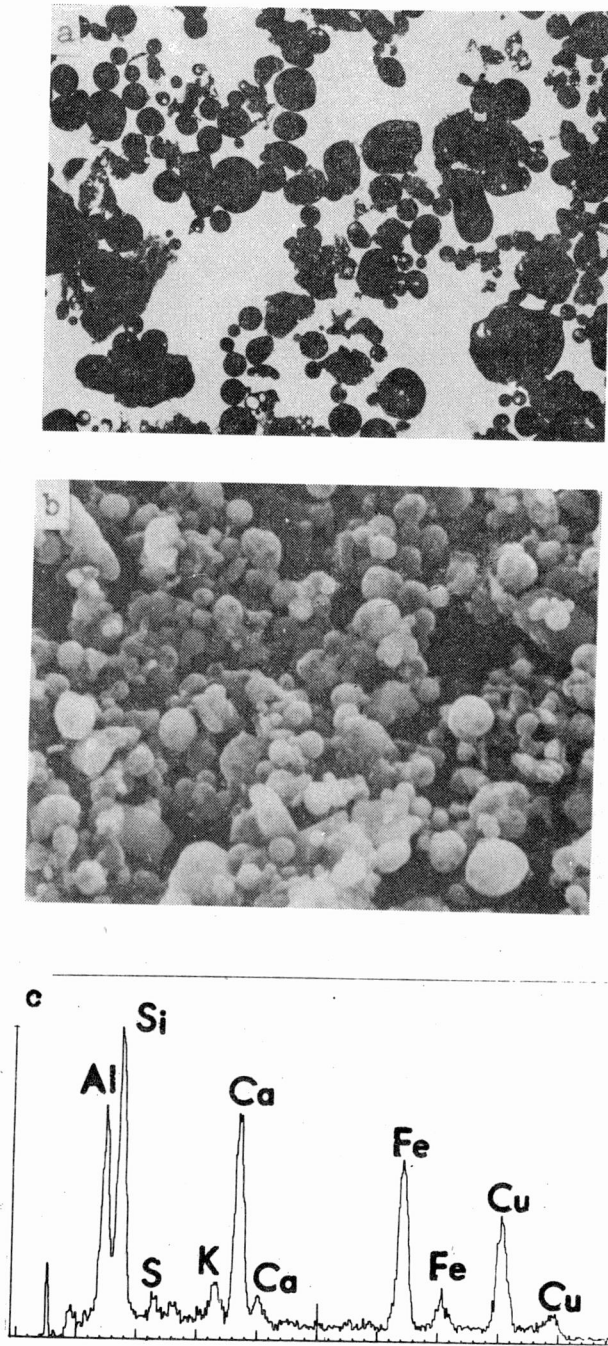


Fig. 2. Particles of aluminosilicates from plant T  
a) TEM, 1 cm = 3 $\mu$ m; b) SEM, 1 cm = 3 $\mu$ m; c) EDXS

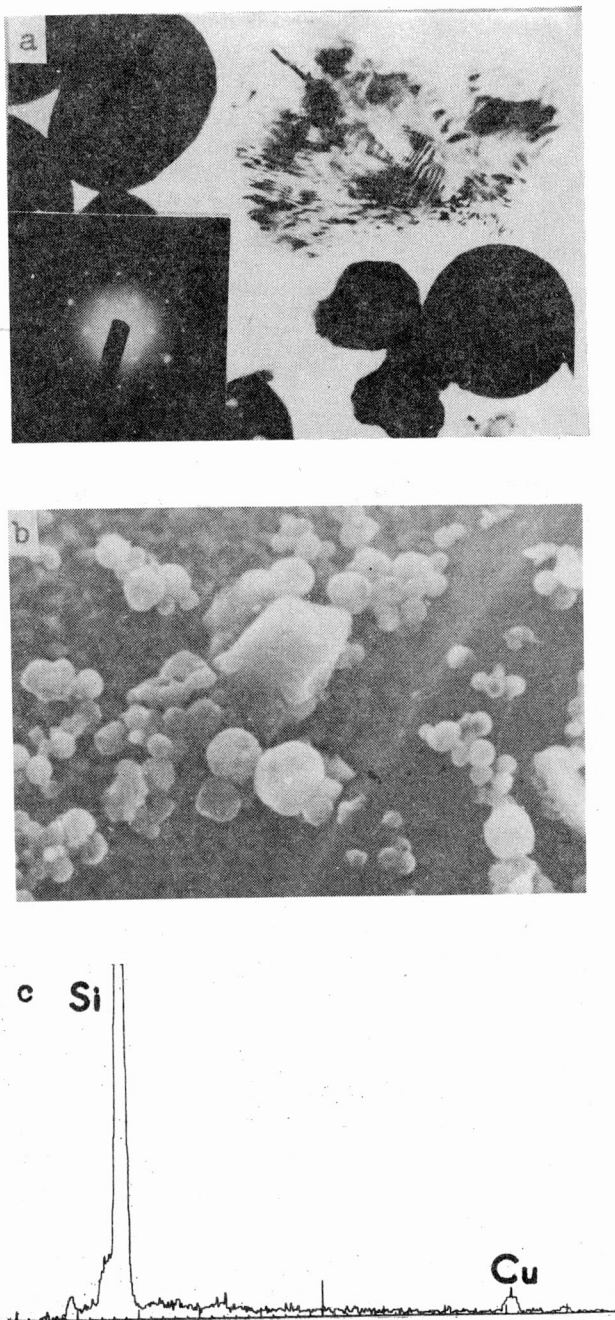


Fig. 3. Particles of quartz from plant T  
a) TEM (SAED), 1 cm = 0,4  $\mu\text{m}$ ; b) SEM, 1 cm = 3  $\mu\text{m}$ ; c) EDXS

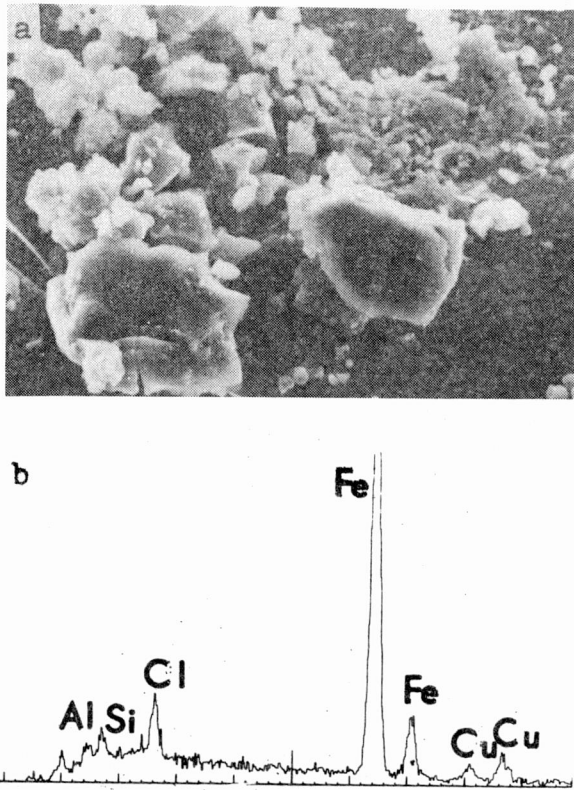


Fig. 4. Particles of iron compounds from plant T

a) SEM, 1 cm = 10  $\mu$ m; b) EDXS

release to form a large number of very small particles which coagulated. Some of the submicron particles volatilized in the furnace and then condensed in the convection furnace, where temperature decrease to 643–823 K. Absence of diffraction of fine particles in our study indicates a glass structure. There are also particle types coming from plant T, e.g., particles of Ti compounds. But these are negligible because of their small contribution. Thus, particle types presented in figs. 2, 3 and 4 may not only be regarded as characteristic of the fine fraction emitted by coal-fired power plants, but also as identifiers of the emission source.

Microscopic examinations have revealed that the particles from aerosol samples collected some 4 km from plant T are identical to those emitted from plant T. There are spherical particles of aluminosilicates (fig. 5a) with no electron diffraction, irregular flakes of quartz (fig. 5b), and particles containing predominantly Fe compounds (figs. 5c, 5d). There were also identified particles of natural and industrial origin. ZWOŹDZIAK [16] and ZWOŹDZIAK et al. [17] discussed them in detail. Some



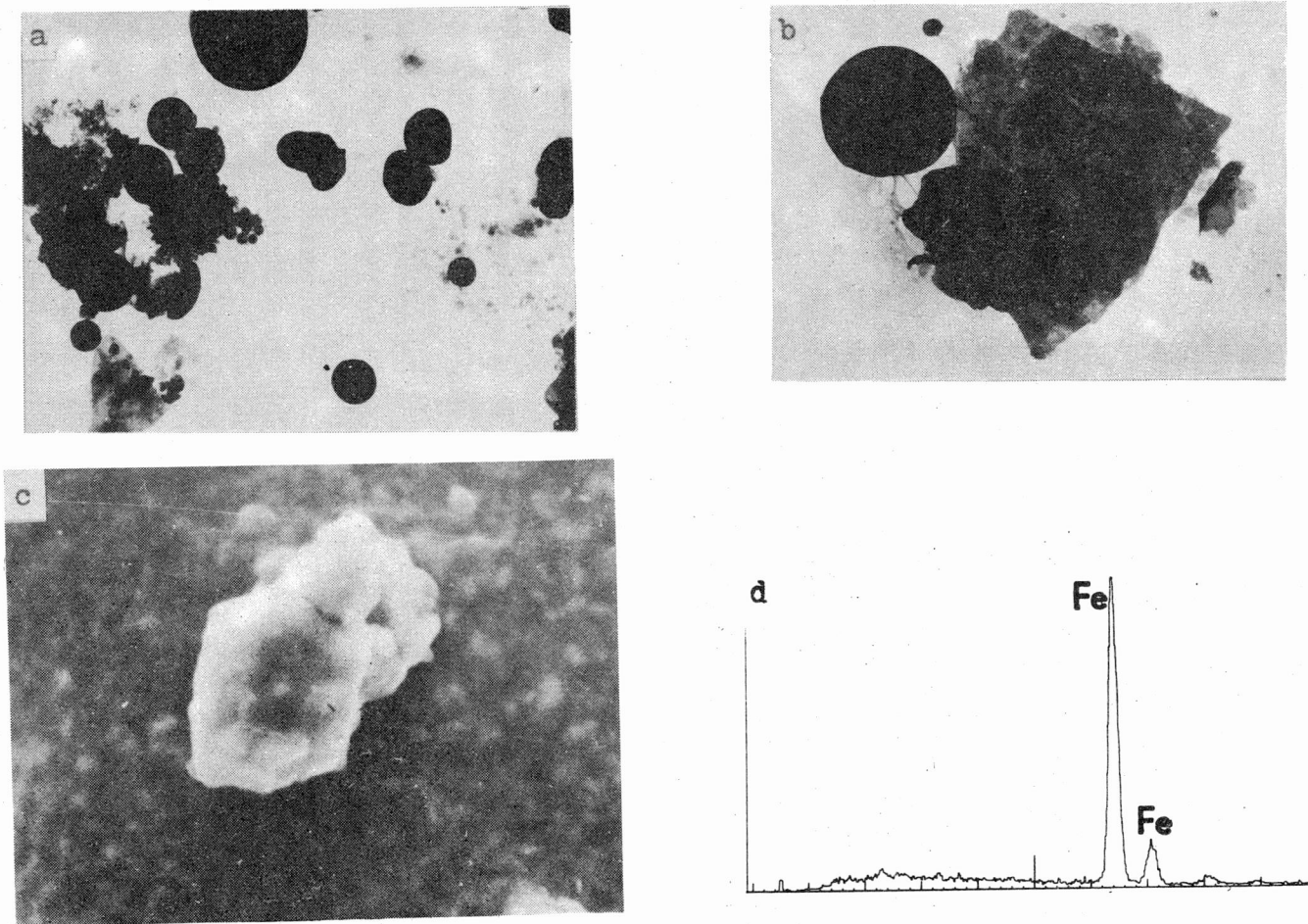


Fig. 5. Particles of aluminosilicates, quartz and iron compounds from aerosol samples collected some 4 km from plant T

a) TEM, 1 cm = 2  $\mu$ m; b) TEM, 1 cm = 0.6  $\mu$ m; c) SEM, 1 cm = 2  $\mu$ m; d) EDXS



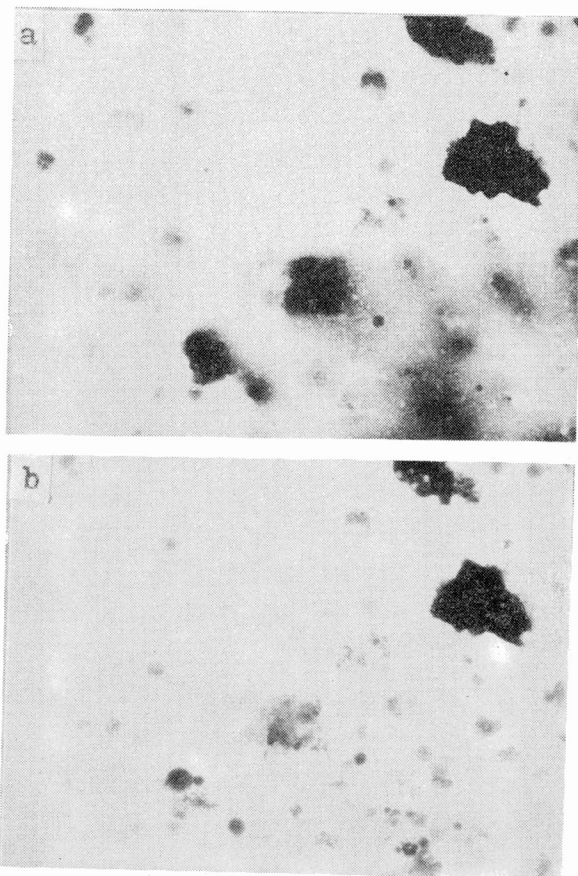


Fig. 6. Particles of ammonium sulphate from aerosol sample collected some 4 km from plant T  
a) TEM, 1 cm = 2  $\mu$ m; b) TEM, 1 cm = 2  $\mu$ m

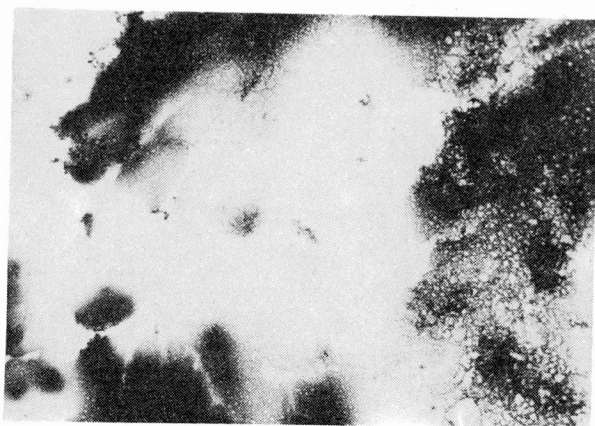
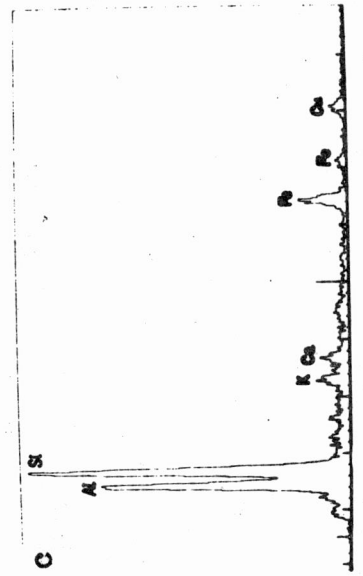
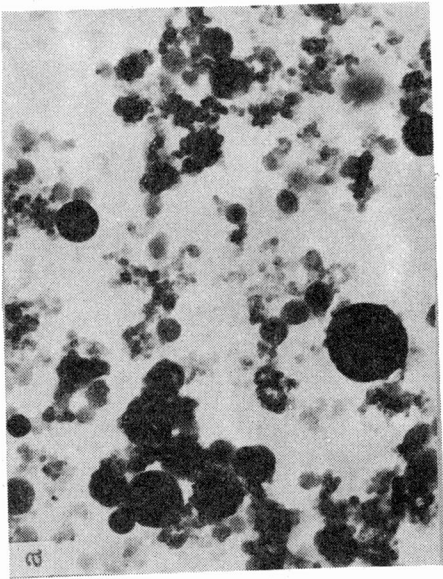
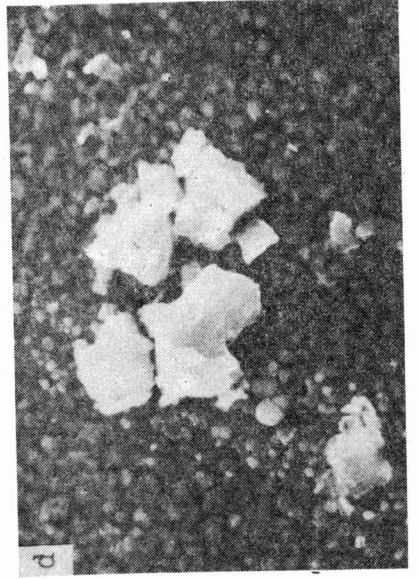
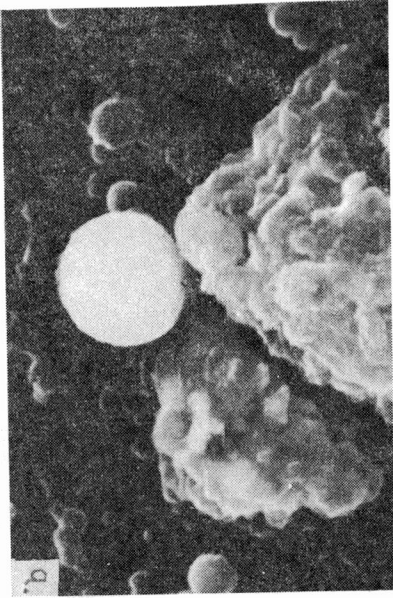


Fig. 7. Standard sample of ammonium sulphate TEM, 1 cm = 3  $\mu$ m



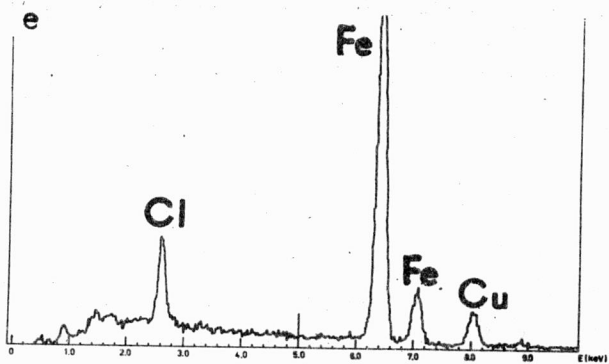


Fig. 8. Particles of aluminosilicates and of iron compounds from aerosol samples collected at the Szrenica summit

a) TEM, 1 cm = 0.6  $\mu$ m; b) SEM, 1 cm = 1  $\mu$ m; c) EDXS; d) SEM, 1 cm = 3  $\mu$ m; e) EDXS

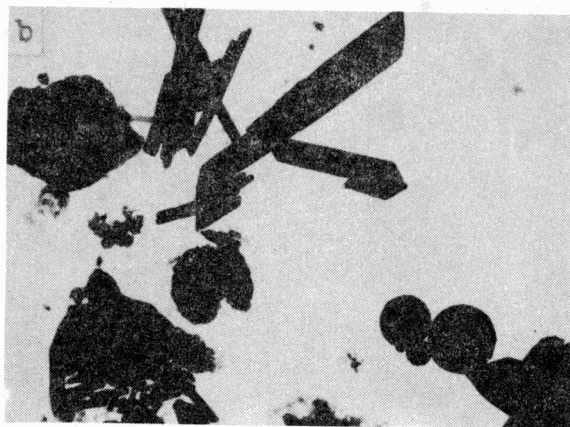
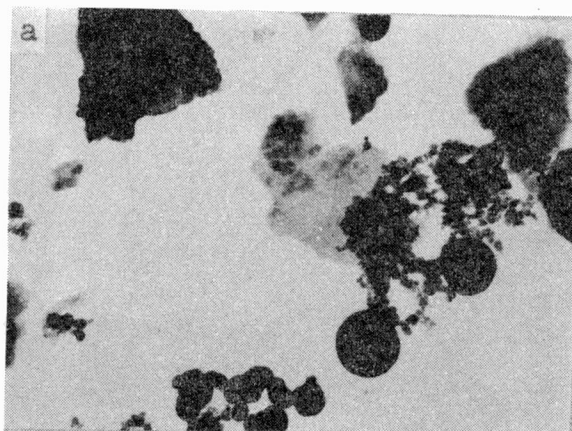
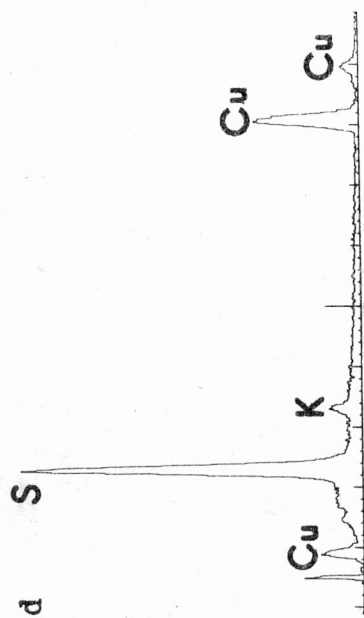
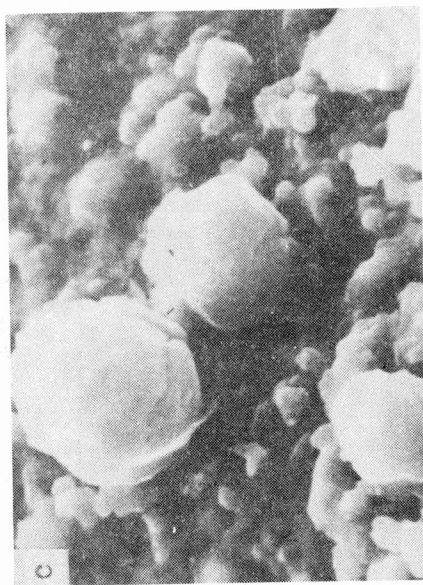
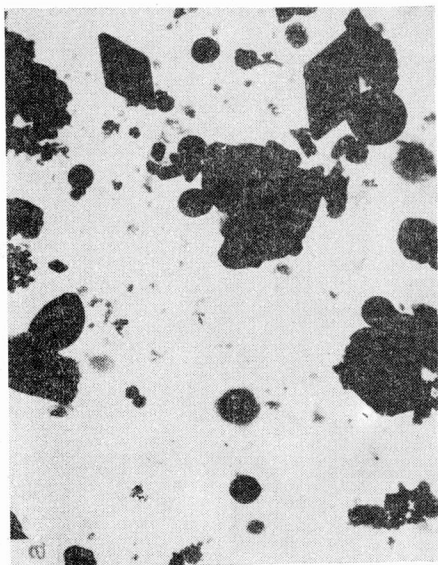
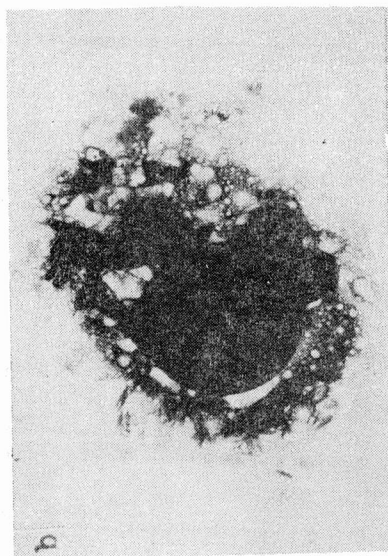


Fig. 9. Particulates collected at the Szrenica summit

a) TEM, 1 cm = 1  $\mu$ m; b) TEM, 1 cm = 3  $\mu$ m



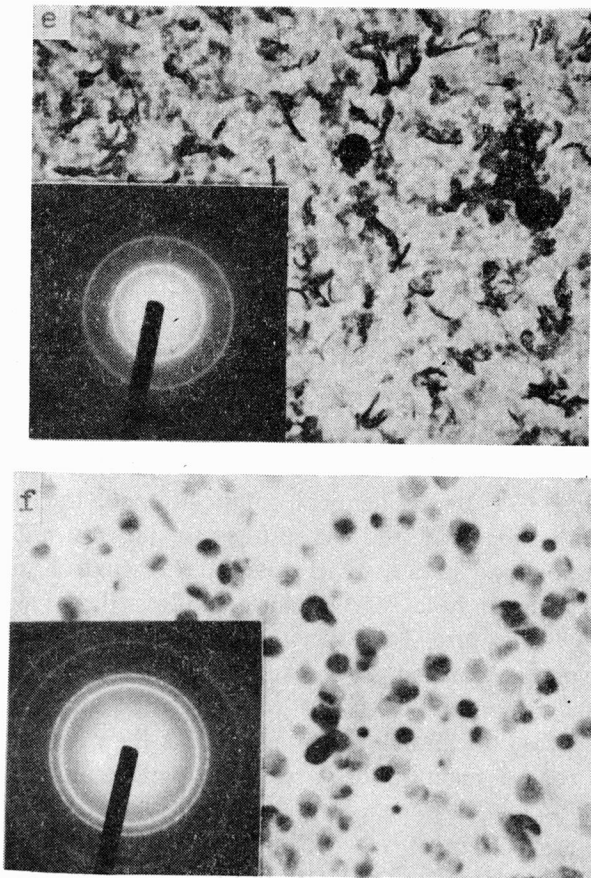


Fig. 10. Particles of ammonium sulphate and layers of crystalline particles identified in aerosol samples collected at the Szrenica summit

a) TEM, 1 cm = 3  $\mu\text{m}$ ; b) TEM, 1 cm = 2  $\mu\text{m}$ ; c) SEM, 1 cm = 3  $\mu\text{m}$ ; d) EDXS; e) TEM (SAED); 1 cm = 0.4  $\mu\text{m}$ ; f) TEM (SAED), 1 cm = 0.1  $\mu\text{m}$

of the preparations display light spots which have not been observed in samples of particles from plant T. The spots were rapidly disappearing in the course of the experiment. Electron diffraction tests have shown the presence of slight reflections exhibiting a crystalline structure. But there was no possibility to record the diffraction pattern on a photographic plate because of the very rapid disappearance of the spots.

The presence of light spots was reported by FERREK et al. [3]; these spots are supposed to be ammonium sulphate particles. To support this hypothesis, a standard sample of ammonium sulphate was prepared. The microscopic image and behaviour of the standard sample are similar to those of the light spots. Hence, they are likely to be ammonium sulphate particles. Figures 6a and 6b show ammonium sulphate particles after exposure to low-intensity electron beam and high-intensity electron

beam, respectively. Standard ammonium sulphate after exposure to low-intensity electron beam is given in fig. 7 for comparative purpose. Ammonium sulphate is a secondary air pollutant, and its identification is helpful in analysing the transformations of air pollutants.

Another sampling site was located at a farther distance from the emission source, at the summit of Szrenica (1362 m a.s.l.). Characteristic spherical particles of aluminosilicate (0.2 to 5  $\mu\text{m}$  diameter) are presented in fig. 8a. The sphere shown in fig. 8b is aluminosilicate (EDXS, fig. 8c) from a coal-fired power plant. The particles in fig. 8d are iron compounds and similar in shape to the particles emitted by a coal-fired power plant (EDXS, fig. 8e). The particles in figs. 9a and 9b differ in shape, size, structure and chemical composition. Some of them have been identified recently by ZWOŹDZIAK [16] and ZWOŹDZIAK et al. [17]. In the aerosol sample from the summit of Szrenica there are also ammonium sulphate particles in droplet form (fig. 10a). Ammonium sulphate generally occurs in the presence of solid particles, e.g., aluminosilicates (figs. 10b, 10c). Chemical composition of the surface layer of the particle in fig. 10c was analysed, and the results are shown in fig. 10d. At increased air humidity continuous layers of a structure similar to that of ammonium sulphate have a tendency to form on holey-carbon support films (the decomposition product exhibit a crystalline structure, figs. 10e and 10f).

Continuous layers are formed on the support films when ammonium sulphate droplets deliquesce and combine with the "wet" envelope surrounding each particle.

The variety of these continuous layers, as well as their similarity to ammonium sulphate, indicate that a reaction of gases with particulates in the atmosphere occurs.

#### 4. CONCLUSIONS

The identification of particulates from a lignite-fired power plant, as well as of airborne ammonium sulphate by microscopic and diffraction methods, has supported their utility when applied to the source apportionment and/or to the investigation of the transformation of air pollutants during long-range transport.

But at this stage of the study it is impossible to interpret all of the diffraction patterns, because the available data sets are incomplete.

The study is underway with the aim to identify as many airborne pollutants as possible and, consequently, to indicate their emission source.

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#### IDENTYFIKACJA CZĄSTEK PYŁÓW LOTNYCH EMITOWANYCH DO ATMOSFERY

Przedstawiono możliwości zastosowania metod mikroskopowych i dyfrakcyjnych do identyfikacji cząstek pyłów lotnych emitowanych z elektrowni węglowej i cząstek z aerozolu atmosferycznego. Cząstki emitowane z elektrowni opalanej węglem brunatnym pobrano w jej sąsiedztwie, cząstki z aerozolu natomiast w odległości 4 km od elektrowni oraz w punkcie pomiarowym położonym na wysokości 1362 m n.p.m.

W badaniach wykorzystano transmisyjny mikroskop elektronowy (określenie wielkości i kształtu cząstek o średnicach  $> 0,1 \mu\text{m}$ , a także ich struktury metodą dyfrakcji elektronowej) oraz analizujący mikroskop elektronowy sprzężony z mikroanalizatorem rentgenowskim (określenie wielkości, kształtu, charakteru powierzchni cząstek o średnicach  $> 1,0 \mu\text{m}$  i ich składu pierwiastkowego).

#### ИДЕНТИФИКАЦИЯ ЧАСТИЦ ЛЕТУЧИХ ПЫЛЕЙ, ЭМИТИРУЕМЫХ В АТМОСФЕРУ

Представлена возможность применения микроскопических и дифракционных методов для идентификации частиц летучих пылей, эмитируемых из угольной электростанции и частиц из атмосферного аэрозоля. Частицы, эмитируемые из электростанции, отапливаемой бурным углем, отобраны в её соседстве, частицы аэрозоля — в расстоянии 4 км от электростанции, а также в измерительной точке находящейся на высоте 1362 н.у.м.

В исследованиях использован трансмиссионный электронный микроскоп (определение размера и формы частиц диаметра  $> 0,1 \mu\text{m}$ ), а также электронный анализирующий, сопряжённый с рентгеновским микроанализатором (определение размера, формы, характера поверхности частиц диаметров  $> 1,0 \mu\text{m}$  и их элементарного состава).