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COMPOSITION OF SIZE-FRACTIONATED AEROSOL IN KATOWICE

39 cascade impactor samples were collected between October 15, 1979 and January 7, 1980 in Katowice. The concentrations of 25 trace elements were measured by means of proton-induced X-ray emission (PIXE) analysis. Enrichment factors relative to the average crustal rock and/or the average stone coal from the Katowice region were calculated. The results indicated that both coarse ($> 1 \mu\text{m}$ EAD) and fine ($< 1 \mu\text{m}$ EAD) fractions of Mg, Al, Si, Ca, Ti, Ni, and Sr as well as the coarse fractions of S, Cl, K, V, Mn, Cu, Zn, Ga, As, Se, Br, Rb, and Pb could be attributed to the coal-related sources. The fine fractions of the latter elements seemed, however, to be related to high temperature industrial processes other than coal combustion.

1. INTRODUCTION

In the study of atmospheric aerosols the distribution of elemental composition with particle size is a frequently measured property which may be important for a number of reasons. One of the reasons is that absorption of airborne trace elements via the respiratory tract and its consequences for human health depend on the size distribution of the particles with which they are associated. In addition to biological effects the size of aerosol particles governs its impact on visibility reduction, affects particle-particle and particle-gas interaction, determines its potential for long-range transport and indicates the possible sources.

Despite the importance of the subject, size distribution data are practically nonexistent in Poland. Most analyses, which are routinely carried out, provide information about total suspended particulates (TSP) and concentrations of some selected elements (Zn, Pb, Fe, Mg, Cu, Mn, and Cd) in airborne particles [1], [2] in order to compare them with the national permissible standards [3].

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Since these regulations are concentrated solely on absolute amounts of TSP (in ng/m^3) or on some selected elements, the control efforts are directed primarily toward the removal of larger, more massive particles that comprise most of the total mass. There is a growing evidence, however, that the smaller particles, although representing a small fraction of the total mass, present the greatest potential health hazard [4] because of their longest atmospheric residence times, most efficient deposition in lung and due to the highest concentration of some potentially toxic elements, many of which appear to be surface deposited [5], [6]. Because the principal particulate emission control technologies, electrostatic precipitators (ESP) and wet scrubbers have low collection efficiency for smaller particles [7], [8], much of the released particles are in the "respirable" size range (equivalent aerodynamic diameter, EAD $< 10 \mu\text{m}$). The effectiveness of future regulations designed to limit the impact of the particles on the public health would be greatly enhanced if the sources and the relative emission rates of these pollutants were known.

As an initial step in filling this gap, air sampling programme was performed in Katowice in order to measure particle size distributions in the ambient air. The particle size distributions of 22 elements were determined by PIXE method in 39 cascade impactor samples collected during one week of October 1979 (15–22) and two weeks of the subsequent winter (December 21, 1979 through January 7, 1980).

2. EXPERIMENTAL

Sampling took place at the Institute of Physics, Silesian University, over a period of 3 weeks. The single orifice cascade impactor [9], which was operated at 1.3 l/m flow rate, separated the particles into 6 size fractions of the following aerodynamic diameters: stage 1, $> 4 \mu\text{m}$, stage 2, $4\text{--}2 \mu\text{m}$, stage 3, $2\text{--}1 \mu\text{m}$, stage 4, $1\text{--}0.5 \mu\text{m}$, stage 5, $0.5\text{--}0.25 \mu\text{m}$, equivalent aerodynamic diameter (EAD), by impaction and stage 6, $< 0.25 \mu\text{m}$ by a $0.4 \mu\text{m}$ pore size Nuclepore filter. Impactor stages were $2.5 \mu\text{m}$ thick Mylar coated with vaseline (stages 1–4) or paraffin (stage 5) to enhance the particle retention. During the first week the cascade impactor was operated for ~ 8 hours and average volume of $\sim 0.6 \text{m}^3$ of air was sampled. When the first analyses of the cascade impactor samples were done an average volume of $\sim 0.2 \text{m}^3$ of air proved to be sufficient for the PIXE analysis and a shorter sampling time was then adopted.

Elemental analyses of each impactor stage and back-up filters were performed by proton-induced X-ray emission (PIXE) at the cyclotron facility of the University of Ghent, Belgium [10]. For the analyses of back-up filter and of the impaction stages 1 and 2 a beam area at the target of 0.18cm^2 was used. These samples were bombarded for a preset charge of $10 \mu\text{C}$ at a beam current $20\text{--}60 \text{nA}$. The count

rate was kept below 2500 cps in order to avoid the occurrence of too many sum peaks. For the analyses of the stages 3 to 5 the beam area was reduced to 0.036 cm². The use of this smaller beam size was possible as the aerosol particle spot for the fine particle stages was confined to a much smaller area than that for the first two stages. The preset charge for stages 3 to 5 was 4 μ C.

Analyses of the PIXE spectra were done by an iterative least square method using the computer code AXIL [11]. Quantitation was based on the homogeneous standard samples, obtained by vacuum deposition of elements or compounds on a Mylar substrate [12]. The concentrations of 25 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, V, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Pb, and Bi) have been measured as a function of aerosol particle size.

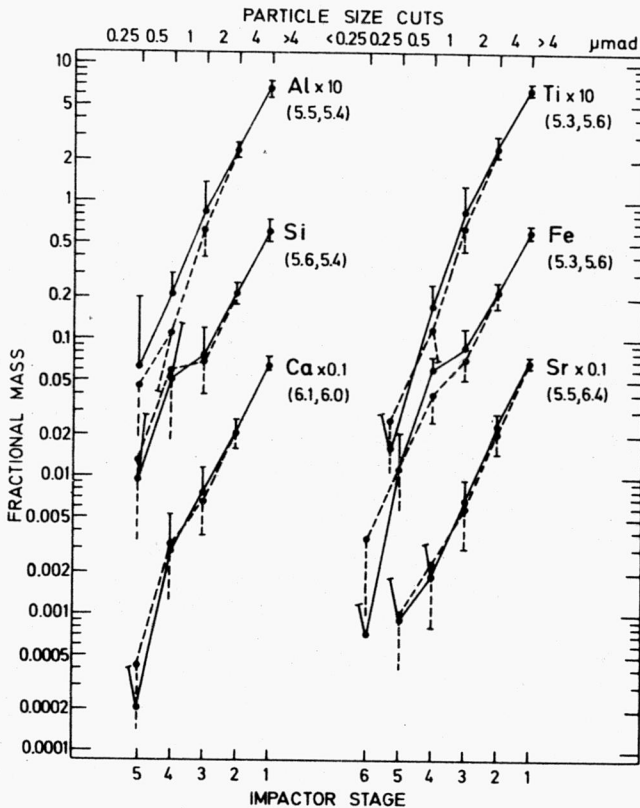


Fig. 1. Average size distributions for Al, Si, Ca, Ti, Fe, and Sr

Mean fraction per stage and standard deviation is indicated for October samples (full lines) and mean fraction minus standard deviation for December-January samples (dashed lines). Error bars without horizontal dash are longer than indicated

3. RESULTS AND DISCUSSION

3.1. PARTICLE SIZE DISTRIBUTIONS

The elemental size distribution data obtained from cascade impactor samples were first normalized to the total element mass summed over all stages for each sample and subsequently averaged over the October and December–January samples, respectively. The mean size distributions for the elements associated with large, medium and small particles are shown in figs. 1–3. The mass median diameters (MMDs) for both sampling periods, obtained by plotting the cumulative size distributions on log-probability paper and interpolating between or extrapolating from the 2 data points closest to the 50% cumulative mass, are listed below the elemental symbols.

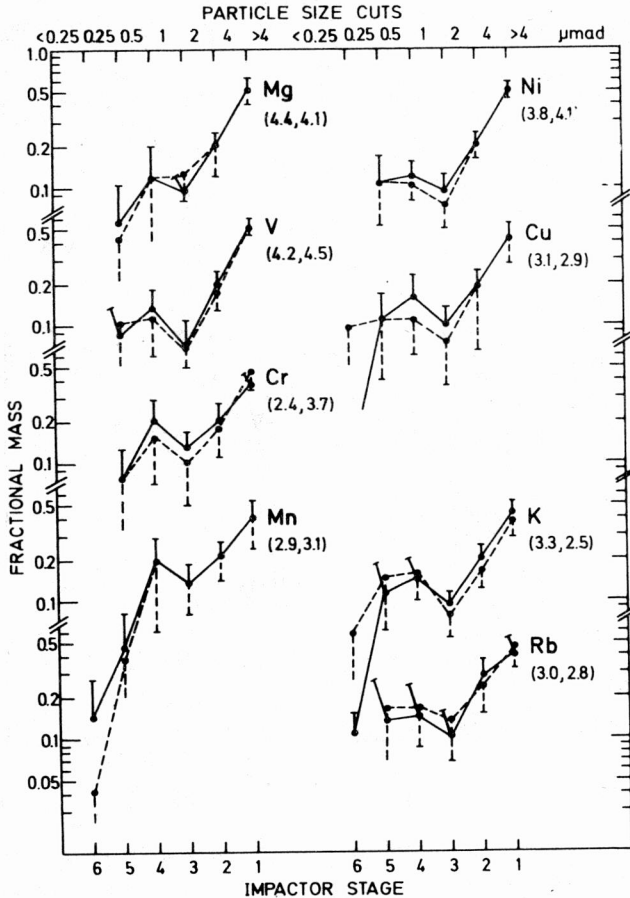


Fig. 2. Average size distributions for Mg, V, Cr, Mn, Ni, Cu, K, and Rb

Figure 1 groups the elements which are predominantly associated with large particles and have virtually unimodal size distributions. There is some indication of a secondary fine mode with the centre at about 0.5–1 μm for Fe and Si. All elements grouped in fig. 1 have their MMDs at about 5 μm . However, it is also quite possible that the MMDs of these large particle elements are systematically too low because of the fact that the particles larger than a few μm were collected by the cascade impactor with very low efficiency [13]. A proper isokinetic sampling of the largest aerosol particles should raise the largest MMDs considerably, probably close to Whitby's MMDs of 10–20 μm EAD for the coarse aerosol mode [14].

Figure 2 presents the medium particle elements having a bimodal size distributions with a secondary fine mode at about 0.5–1 μm EAD. In the true bimodal size distribution the element in question has multiple well-defined source processes which yield differently sized particles containing the element. The final MMD of the element will depend on the relative strength of the various sources.

Figure 3 groups the size distributions of relatively volatile elements which have the MMDs of the order of $\sim 1 \mu\text{m}$ EAD. They all show a bimodal distribution with

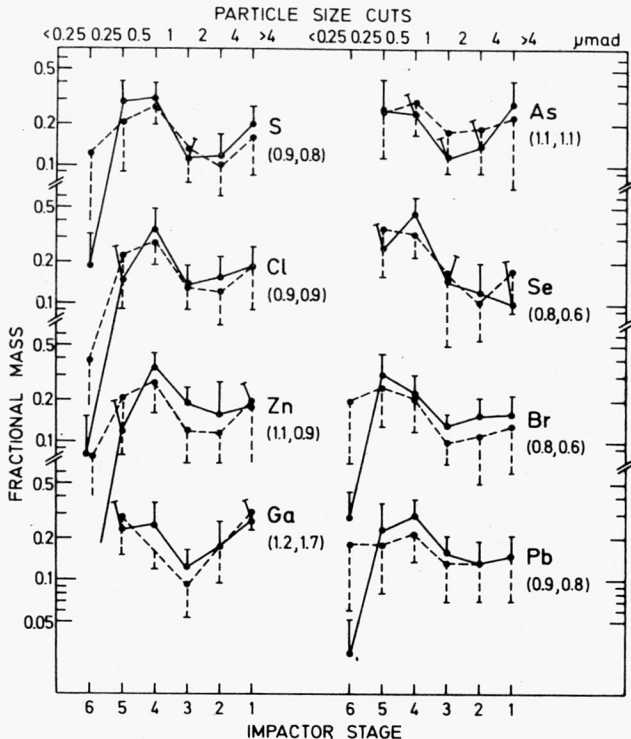


Fig. 3. Average size distributions for S, Cl, Zn, Ga, As, Se, Br, and Pb

the maximum concentration in the 0.5–1 μm EAD range. This range was also the most visibly black in all samples implying the presence of soot carbon particles.

Table 1 lists the mass median diameters (MMDs) averaged over the two sampling periods together with the reported range from elsewhere [15]. Only Ni and Pb lie outside the reported range and of these Pb is reasonably close.

Table 1

Mass median diameters of trace elements in the atmospheric aerosol of Katowice and the reported ranges

Element	MMD (μm)	Reported range (μm)
Mg	4.2	3–8
Al	5.5	3–9
Si	5.5	—
S	0.85	—
Cl	0.85	0.4–0.9
K	2.9	1–7
Ca	6.0	4–8
Ti	5.4	2–9
V	4.3	0.4–5
Cr	3.0	1–8
Mn	3.0	1–7
Fe	5.4	1.5–6
Ni	3.7	0.6–1.5
Cu	3.0	0.6–7
Zn	1.0	0.7–8
Ga	1.4	0.7–3
As	1.1	0.6–3
Se	0.7	0.5–3
Br	0.7	0.2–3
Rb	2.9	—
Sr	5.9	—
Pb	0.85	0.2–0.7

3.2. COARSE AND FINE PARTICLE MODE COMPOSITION

According to the MMDs (tab. 1) the elements measured can be broadly classified into two categories:

- 1) coarse particle elements with MMDs $> 1 \mu\text{m}$ EAD which include Mg, Al, Si, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Rb, and Sr,
- 2) fine particle elements with MMDs $< 1 \mu\text{m}$ EAD including S, Cl, Zn, Ga, As, Se, Br, and Pb.

Table 2 summarizes the concentrations of the coarse particle elements as a function of particle size. As could be expected from the average distributions (fig.

Table 2

Mean concentration of the coarse particle elements in the different size fraction

Element	Average concentration (ng·m ⁻³)					
	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6
Mg	190±110	80±60	56±50	57±78	16±18	120±70
Al	2860±1530	1120±680	270±150	97±260	15±19	160±380
Si	5100±2870	1920±1150	580±400	814±1800	150±320	240±570
P	34±21	13±13	9±12	7.5±5.5	9±6	124±230
K	800±410	350±185	160±80	330±200	280±200	150±513
Ca	2250±1380	730±530	260±280	117±180	11±10	18±38
Ti	210±100	75±40	19±9	3.4±1.5	0.6±0.4	3.5±6.1
V	10±5	3±2	1.3±0.6	1.9±0.8	1.7±1.3	18±28
Cr	23±30	10±14	4.6±5.1	6.2±5.8	2.6±3.4	15±40
Mn	150±190	70±80	46±50	90±170	15±30	155±600
Fe	3070±1500	1040±550	345±200	190±110	50±45	150±600
Ni	9±8	3±2	1.1±0.7	1.6±0.9	1.8±1.8	4±7
Cu	24±30	13±15	5±3	6.3±3.3	6.6±4.8	7.0±11.7
Rb	5±3	3±2	1.5±1.0	1.9±1.0	1.7±1.7	3.8±3.5
Sr	30±19	9±6	2.2±1.3	0.7±0.5	0.3±0.3	3.9±5.2

Table 3

Mean concentration of the fine particle elements in the different size fraction

Element	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6
S	645±480	400±260	530±340	1000±470	670±350	440±380
Cl	955±990	600±510	600±390	1240±580	920±570	160±260
Zn	490±1520	155±330	106±130	170±90	109±60	49±55
Ga	2.4±1.5	1.3±1.0	0.7±0.4	1.1±0.5	1.8±1.0	1.8±2.4
As	4.3±3.9	3.3±3.5	3.1±3.0	4.7±3.1	3.5±1.8	3.0±3.2
Se	3.6±6.3	2.0±3.5	5.1±11	7.9±20.7	2.3±2.2	1.0±0.5
Br	22±29	20±28	14±20	21.2±9.5	24±11	32±38
Pb	150±210	135±180	130±200	140±114	93±50	120±130
Bi	3.3±3.3	2.3±1.9	1.5±2.3	1.7±1.4	1.4±0.8	2.5±2.1

1), the concentrations of Al, Si, Ca, Ti, Fe, and Sr decrease dramatically with the increasing stage number. Only 5% of the total aerosol mass of these elements is found in fine particle mode (stages 4–6).

The elements associated with medium and small particles are about equally distributed between the two size fractions (tab. 3) with a tendency towards significant elemental concentrations in the fine particle mode, especially for S, Cl, Br, and Pb.

Table 4 presents the average elemental composition of coarse and fine particle fractions for October and December–January samples. Although the absolute

Table 4

Coarse and fine mode aerosol composition

Element	Average percentage \pm standard deviation			
	Coarse fraction 1 μm EAD		Fine fraction $\leq 1 \mu\text{m}$ EAD	
	October	Dec.-Jan.	October	Dec.-Jan.
Na	1.1 \pm 0.8	0.8 \pm 0.9	23.3 \pm 4.9	17.4 \pm 5.6
Mg	1.5 \pm 0.2	1.2 \pm 0.3	1.1 \pm 0.4	1.6 \pm 1.5
Al	13.8 \pm 3.3	15.6 \pm 4.2	1.3 \pm 0.5	1.5 \pm 2.2
Si	26.3 \pm 5.7	27.8 \pm 8.1	5.6 \pm 8.4	8.1 \pm 11.2
S	6.8 \pm 5.1	5.9 \pm 2.6	22.6 \pm 7.4	23.6 \pm 6.7
Cl	5.7 \pm 1.9	7.6 \pm 3.2	21.3 \pm 9.3	24.7 \pm 6.8
K	5.1 \pm 0.9	4.9 \pm 1.0	5.6 \pm 1.8	7.3 \pm 1.7
Ca	16.0 \pm 5.5	12.5 \pm 6.6	2.2 \pm 2.4	1.7 \pm 2.3
Ti	1.1 \pm 0.4	1.1 \pm 0.3	0.07 \pm 0.05	0.07 \pm 0.09
V	0.06 \pm 0.01	0.05 \pm 0.02	0.05 \pm 0.02	0.04 \pm 0.01
Cr	0.12 \pm 0.11	0.13 \pm 0.17	0.12 \pm 0.08	0.11 \pm 0.12
Mn	0.6 \pm 0.5	0.9 \pm 1.0	0.8 \pm 1.0	0.9 \pm 1.1
Fe	16.7 \pm 4.0	16.9 \pm 4.6	4.0 \pm 2.0	3.4 \pm 2.7
Cu	0.14 \pm 0.07	0.19 \pm 0.15	1.6 \pm 0.07	0.2 \pm 0.1
Zn	3.0 \pm 3.2	2.1 \pm 4.1	6.8 \pm 6.6	3.5 \pm 1.1
Pb	1.6 \pm 2.2	1.5 \pm 2.0	3.6 \pm 2.1	4.1 \pm 3.0

elemental concentrations vary by one order of magnitude, the inter-element ratios are quite consistent over the two sampling periods. Especially Al, Si, Ti, Ca, and Fe seem to be associated with each other and their relative abundances in coarse and fine mode remain constant within the standard deviation which is of the order of 30%.

Between the coarse and fine fractions there appear clear cut differences. In the coarse mode the major lithophilic elements (Mg, Al, Si, Ca, Ti, and Fe) account for $\sim 75\%$ of the total coarse particle mass, whereas in the fine particle mode their concentrations are much smaller ($\sim 5\%$ of the total mass). On the other hand, the fine particle fraction is dominated by the presence of S and Cl which account for about 43% of the total fine particle mass.

3.3. ENRICHMENT AS A FUNCTION OF PARTICLE SIZE

Aerosol-crust enrichment factors (EFs) relative to Fe and to average crustal rock composition [16] (tab. 5) were calculated according to the equation:

$$EF_{\text{Fe,rock}} X = \frac{X/\text{Fe}_{\text{impactor stage}}}{X/\text{Fe}_{\text{rock}}}$$

The average enrichment factors for different particle sizes are summarized in fig. 4. It appears that enrichment as a function of particle size for elements having virtually unimodal size distribution (fig. 1) is distinctly different from that for the elements displaying bimodal distribution and associated with medium and small particles of aerosol (figs. 2 and 3). Al, Si, Ca, Ti, Rb, and Sr, which have their EFs close to unity, do not vary in enrichment with the particle size. Only a slight increase of EF on the back-up filter is observed.

The elements with a bimodal size distribution and associated with the finest particles (MMDs $< 3 \mu\text{m}$ EAD) show a significant increase in enrichment with the decreasing particle size. Especially high enrichment factors ($> 10^4$) were found for Pb, Bi, Br, and Se in the finest particle fraction. This is consistent with a general rule [15] that the large particle elements are present in aerosol in nearly crustal proportions and medium-sized and small particle elements are highly enriched.

Table 5

Average amounts of the elements
in crustal rocks in grams per ton
or parts per million

Element	Crustal average
Na	28300
Mg	20900
Al	81300
Si	277200
P	1050
S	260
Cl	130
K	25900
Ca	36300
Ti	4400
V	135
Cr	100
Mn	950
Fe	50000
Co	25
Ni	75
Cu	55
Zn	70
Ga	15
As	1.8
Se	0.05
Br	2.5
Rb	90
Sr	375
Pb	13
Bi	0.2

It is now well established that many trace element species, such as Se, As, Mo, Ga, U, W, the halogens, Hg, Sb, Cd, and Zn emitted from coal-fired power plants are concentrated or enriched on the smaller aerosol particles [7], [17]–[21]. Much of the mass is on the surface of the particle rather than volume distributed [5],

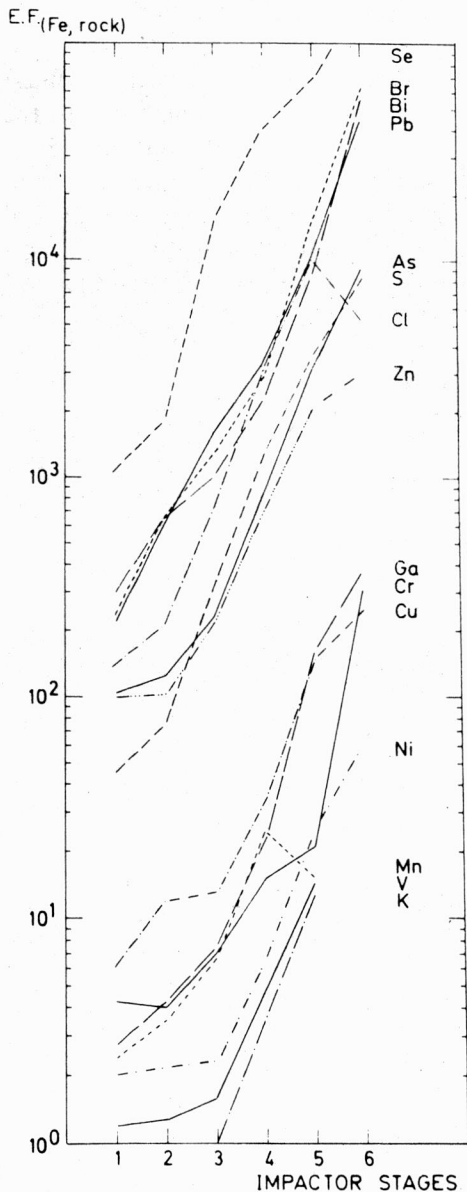


Fig. 4. Elemental enrichment factors (Fe, rock) as a function of particle size

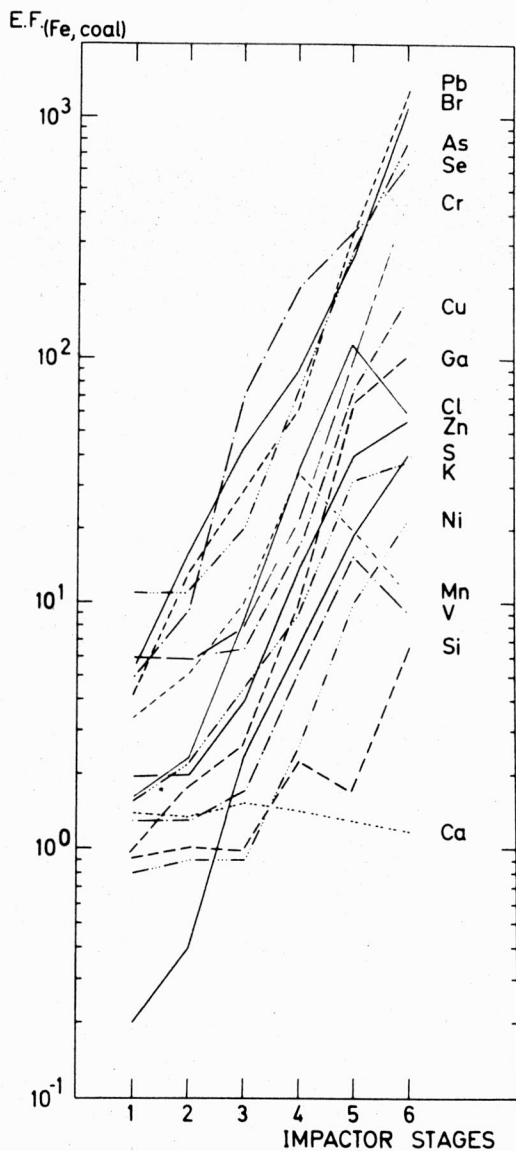


Fig. 5. Elemental enrichment factors (Fe, coal) as a function of particle size

[6]. Surface enrichment of coal combustion ash has generally been attributed to adsorption/condensation processes. That means that surface enrichment occurs because the trace and minor elements or their compounds are volatilized in the high temperature zone of the combustor being subsequently adsorbed or condensed onto the entrained aluminosilicate ash particles [17]. Since condensation and adsorption are surface phenomena, the concentration of condensed elements should be inversely proportional to particle size. Although adsorption/condensation undoubtedly contributes to the observed surface enrichment, other processes, such as surface segregation, have been recently taken into account [22]. Many of the trace and minor elements, which are present in the aluminosilicate inclusions in the coal, can enrich the surface of the ash particles because of diffusive transport of these elements to the surface of the ash particle (i.e., surface segregation) occurring at the elevated temperatures experienced during and after combustion process.

Recent studies also indicate that elemental surface predominance may be a general phenomenon occurring in airborne particles derived from high temperature combustion operations [23]–[26].

The predominance of certain elements in small particles is significant in determining the degree of enrichment of these elements in urban aerosol. As small particles can travel very long distances and have very large residence times, the elements associated with these particles highly enriched in the aerosol would be expected.

As coal combustion does indeed control the abundances of many elements in urban aerosol of Katowice [27], aerosol–coal enrichment factors relative to Fe and average hard coal composition from Katowice region (tab. 6 [28]) were calculated as:

$$EF_{\text{Fe, coal } X} = \frac{X/\text{Fe}_{\text{impactor stage}}}{X/\text{Fe}_{\text{coal}}}$$

The results are given in fig. 5. The overall form of the EFs' dependence on particle size is very similar for both enrichment factors (figs. 4 and 5). The elements highly enriched in aerosol relative to the crustal rock remain enriched relatively to coal. However, the absolute values of EFs (Fe, coal) are by one or two order of magnitude smaller than EFs (Fe, rock). This suggests that coal combustion can account for a large part of atmospheric enrichment of the elements considered.

It should be pointed out, however, that elemental enrichment relative to hard coal composition occurs more likely in fine particle mode (stages 4–6), while in coarse particle mode (stages 1–3) even the elements normally considered as highly enriched (S, Cl, Zn) have their EFs close to unity or only moderately high (~10).

Figure 6 is a log-log plot of the coal enrichment factors versus aerosol enrichment factors calculated with respect to the average crustal rock composition

for fine and coarse elemental modes. As the degree of enrichment in coal is roughly proportional to that in atmosphere but of a power less than one [15] an envelope of constant width and slope $2/3$ is also drawn in fig. 6. For some elements (i.e., Mg, Al, Si, Ti, Ca, Ni, and Sr) the aerosol enrichment factors for both fine and coarse fractions are situated well inside the envelope. For the elements, like Na, K, V, Mn, Cu, Zn, As, Pb, and perhaps Cr, only coarse particle fraction can be attributed to the coal combustion.

It is also interesting to note the presence of coarse particles S and Se above the envelope. This can be interpreted as depletion in the urban aerosol relative to what should be expected from the coal. Indeed, S and Se are two of the five elements which usually show negative mass imbalances in studies of coal-fired power plants [19], [29], which means that the amount of the given element found

Table 6
Mean concentration of the trace elements in the hard
coal samples from the Katowice region [28]

Element	Arithmetic mean	Standard deviation	Number of samples
Na	883.2	554.7	31
Mg	3808.1	2547.7	31
Al	17879.9	16946	31
Si	33197.0	38996.0	31
S	10433.0	6175.0	31
P	555.0	480.0	21
Cl	1341.5	1416.4	31
K	4406.0	5153.5	27
Ca	4910.8	4061.1	20
Ti	952.8	811.3	22
V	33.9	30.4	30
Cr	24.5	25.9	31
Mn	170.0	153.7	31
Fe	11100.5	8475.7	31
Co	11.3	13.9	32
Ni	39.0	30.2	11
Cu	59.7	34.5	10
Zn	242.9	816.9	24
Ga	8.2	5.9	28
As	9.4	16.5	28
Se	2.6	4.3	28
Br	12.8	14.3	30
Rb	4.0	5.2	3
Sr	153.5	103.4	22
Pb	28.0	30.0	30

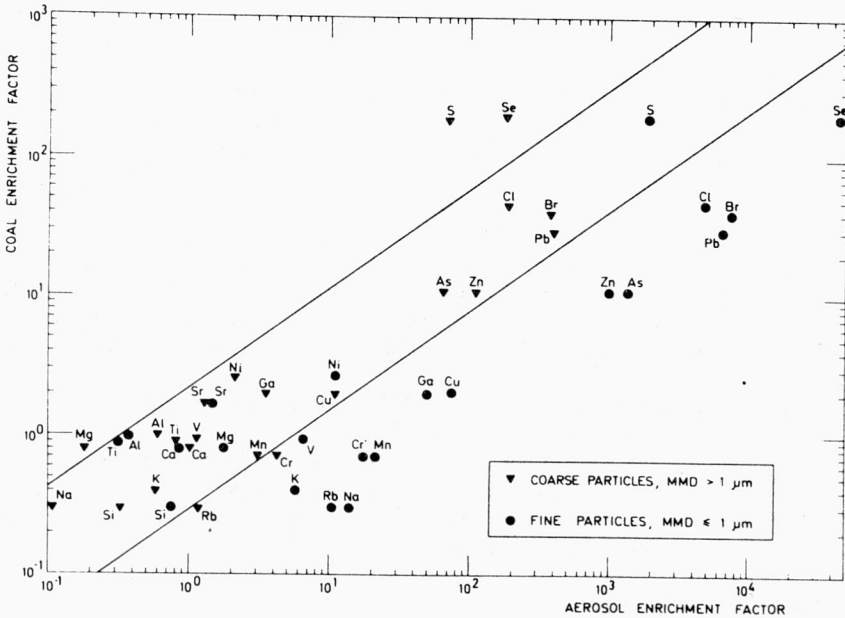


Fig. 6. Enrichment factor in coal versus urban enrichment factor for coarse and fine particle fractions

in the output is smaller than that which has been introduced with the coal. The other elements having negative mass imbalances are Hg, Cl, and Br. By the imbalance we usually mean that the elements leave the stack as vapours.

As fine mode of Na, K, Mn, Cr, Cu, Zn, As, Pb, Se, and S seem to be "too enriched" in the atmosphere — other than coal combustion industrial processes must have been involved in the formation of small particles of these elements.

4. SUMMARY AND CONCLUSIONS

1. Mg, Al, Si, K, Ca, Ti, Fe, and Sr are predominantly associated with large particles (EAD $> 3 \mu\text{m}$) and have virtually unimodal mass-size distributions. These elements account for $\sim 80\%$ of the total coarse particle mass measured in the experiment and their enrichment factors with respect to Fe and average crustal rock composition are close to unity for all size fractions.

2. The remaining elements (S, Cl, V, Cr, Mn, Ni, Cu, Zn, Ga, As, Se, Br, and Pb) associated with medium and fine particles (EAD $< 3 \mu\text{m}$) have bimodal mass-size distributions and show a significantly increasing enrichment with the decreasing particle size. Especially high enrichment factors ($> 10^4$) are found for Pb, Bi, Br, and Se in the finest particle fraction (EAD $\sim 0.5 \mu\text{m}$).

3. The fine fraction (EAD $< 1 \mu\text{m}$) of Na, K, Mn, Cr, Cu, Zn, As, Pb, Se, and S seem to be related to the other high temperature processes than coal combustion.

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SKŁAD FRAKCJONOWANEGO AEROZOLU W KATOWICACH

Zbadano 39 próbek aerozolu pobranych w Katowicach za pomocą impaktora kaskadowego w okresie od 15 października 1979 r. do 7 stycznia 1980 r. Zmierzono stężenia 25 pierwiastków stosując emisyjną analizę rentgenowską (PIXE). Obliczono współczynniki wzbogacenia aerozolu w stosunku do przeciętnego składu skały krystalnej i/lub węgla kamiennego. Uzyskane wyniki wskazują, że zarówno grube ($> 1 \mu\text{m}$) jak i drobne ($< 1 \mu\text{m}$) frakcje Mg, Al, Si, Ca, Ti, Ni i Sr oraz grube frakcje S, Cl, K, V, Mn, Cu, Zn, Ga, As, Se, Br, Rb i Pb pochodzą ze źródeł węglowych. Drobne frakcje drugiego szeregu pierwiastków wydają się być związane z innymi niż wysokotemperaturowe spalanie węgla procesami przemysłowymi.

СОСТАВ ФРАКЦИОНИРОВАННОГО АЭРОЗОЛЯ В Г. КАТОВИЦЕ

Было исследовано 39 проб аэрозоля, отбираемых в г. Катовице с помощью каскадного импактора в период от 15 октября 1979 г. до 7 января 1980 г. Была измерена концентрация 25 химических элементов, применяя эмиссионный рентгеновский анализ (PIXE). Вычислены коэффициенты обогащения аэрозоля по отношению к среднему составу кристаллической породы и/или каменного угля. Полученные результаты показывают, что как крупные ($> 1 \mu\text{м}$), так и мелкие ($< 1 \mu\text{м}$) фракции Mg, Al, Si, Ca, Ti, Ni и Sr, а также крупные фракции S, Cl, K, V, Cu, Zn, Ga, Se, Br, Rb, As и Pb происходят от углеродных источников. Мелкие фракции второго ряда химических элементов кажутся связанными с другими промышленными процессами по сравнению с высокотемпературным сжиганием угля.