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## A METHOD FOR STUDYING THE CONTRIBUTION OF HEAVY METALS IN MARINE AEROSOL DEPENDING ON THE PARTICLE SIZE DISTRIBUTION\*

Contents: 1. Introduction, 2. Sampling method, 3. Spectrophotometric analysis,  
4. Micrometric analysis, 5. Analysis of results; Streszczenie; References

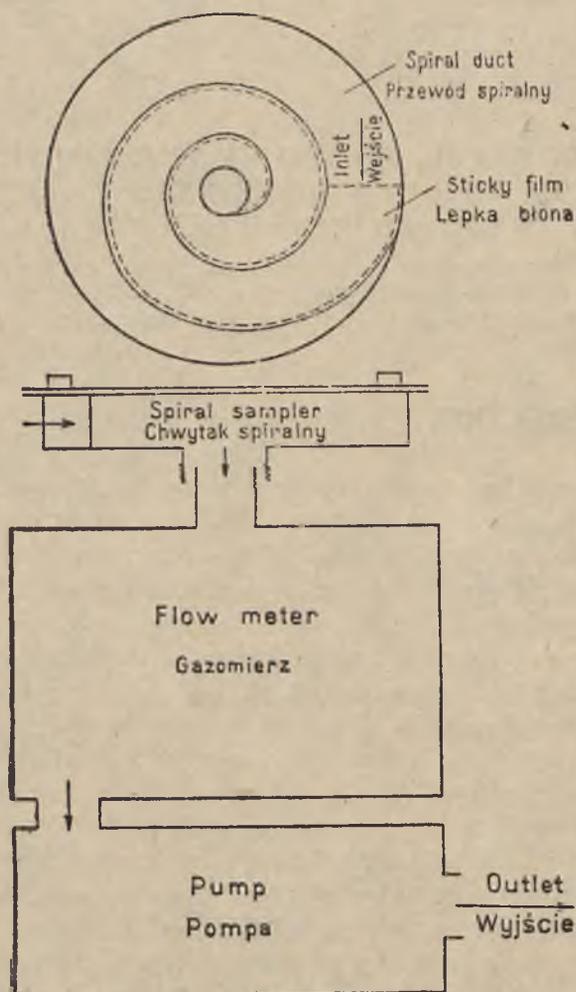
### 1. INTRODUCTION

One of the important problems concerning the transfer of pollutants is the relationship between the concentration of trace elements and their compounds and particle size distribution of the dispersion system. Hoffman and Duce [5] found organic carbon in an oceanic (Samoa Islands, Bermudas, Hawaii) atmospheric aerosol to be bound mostly with particles of a diameter smaller than 0.5  $\mu\text{m}$ . On the other hand, laboratory studies involving the measurement of the carbon content in sea water dispersed in air revealed the bulk of organic carbon to have a particle size ranging from 1 to 3  $\mu\text{m}$ . The concentration of heavy metals and other elements occurring in atmospheric aerosol over marine regions was likewise found to be variously related to particle size distribution [3, 7]. Garbalewski and Berek [4] have suggested differences in the distribution of mercury concentrations in the aerosol when comparing data for the inshore zone in Gdynia with those of distant regions of the Baltic Sea. A relationship can be noted between the metal content and the ratio of presubmicron particles. The relationships can be modified by complicated processes accompanying generation and transfer of suspended matter in the atmosphere [7]. Not only the source of the suspensions themselves [2] but also their residence time in the atmosphere affect markedly the dispersion composition of aerosols [7]. In the above cited article [4] the distribution of mercury concentration was studied over the range of both giant and presubmicron particles. From

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an article by Junge [6] it follows that particles with a radius interval of the order of  $10^{-2}$  to  $10^{-1}$   $\mu\text{m}$  prevail in the atmospheric aerosol.



**Fig. 1. Schematic diagram of the spiral impactor.**  
Outer diameter of the spiral chamber 33 cm; tape length 150 cm; dimensions of the inlet orifice  $4 \times 11$  cm; dimensions of the outlet orifice in the spiral chamber  $4 \times 1$  cm [4].

**Rys. 1. Schemat impaktora spiralnego.**  
Zewnętrzna średnica komory spiralnej — 33 cm, długość taśmy — 150 cm, otwór wlotowy —  $4 \times 11$  cm, otwór wylotowy w komorze spiralnej  $4 \times 1$  cm.

In this connection, the aim of this work was to extend those studies to include the interval of submicron particles.

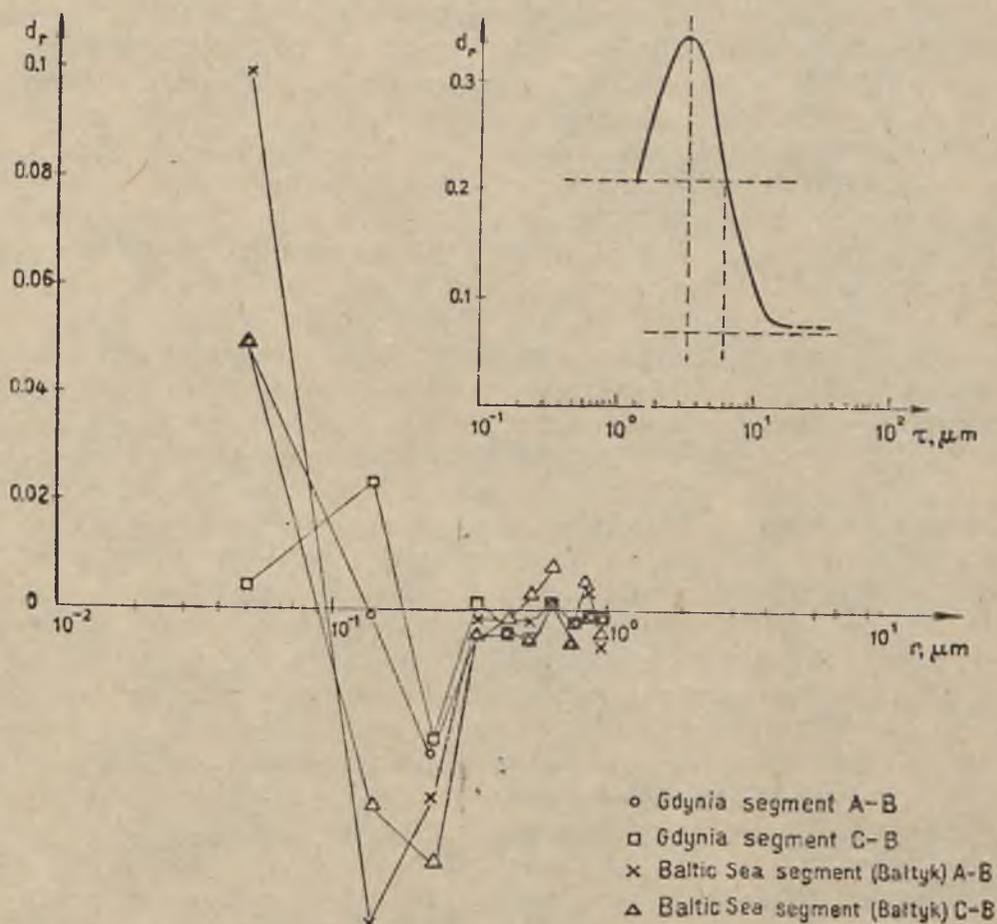


Fig. 2. Distribution of the contribution of submicron particles to various ranges of their size spectrum.

The results refer to samples collected on segments A, B and C of a sticky spiral tape exposed in the spiral impactor. For comparison, in the right-hand corner a distribution curve for mercury on presubmicron particles has been provided [4].

Rys. 2. Rozkład udziału cząstek submikronowych w różnych zakresach widma ich wielkości.

Dane dotyczą prób zebranych na segmentach A, B, C lepkiej taśmy spiralnej eksponowanej w impaktorze spiralnym. W prawym rogu dla porównania przytoczono krzywą rozkładu udziału rtęci na cząstkach, uzyskaną dla cząstek presubmikronowych [4].

## 2. SAMPLING METHOD

Aerosol samples over the range of different particle size intervals were taken by means of a spiral impactor (with a diameter ranging from

33 to 7 cm; Fig. 1) in which the capture of particles was accomplished by centrifugal force. The method had been employed in [4] and consisted in the exposition in the spiral channel of the impactor celluloid tape ( $3.7 \times 150$  cm) coated with a polyacrylic resin of stable viscosity under experimental conditions. At the same time microscopic gauzes were additionally exposed on the tape coated with two sorts of films — a collodion one and a metallic gold foil. Aerosol samples were taken in Gdynia at a height of 18 m a.s.l. In the open Baltic Sea the air was pumped from the top deck of the vessel „Hydromet” at a height of 6 m a.s.l. The sampling was accomplished at a pumping rate of 3000—5000  $\text{cm}^3 \text{s}^{-1}$ .

After exposure the tape was divided into three equal segments. Segment A — the initial segment from the air inlet, 48 cm long; segment B — the middle one, cut at a distance of 48 and 96 cm, and segment C, the final one, situated at a distance of 96 and 144 cm from the inlet. The collecting surface area of each segment was 120  $\text{cm}^2$ . According to a theory advanced in [4] the first segment should catch giant particles under the effect of forces of inertia, although adsorption of the smallest fraction should also be important. On the third segment the influence of the forces of inertia on the remaining particles increases considerably.

To establish relationships between size distribution of submicron particles and the concentrations of mercury and cadmium in the aerosols, they were collected on microscopic gauzes coated with collodion film. The contribution of submicron particles in the transfer of mercury was tried to be determined by means of the metallic gold foil.

To collect sufficiently large samples of suspensions on the spiral tape, about 1000  $\text{m}^3$  of air was pumped. The filtration time was several days. To be able to compare results remote in time, sampling conditions had to be similar. The samples were taken during clear periods.

### 3. SPECTROPHOTOMETRIC ANALYSIS

Aerosol samples were eluted from segments A, B and C with a hot 1:1 nitric acid of spectral purity. At the same time blanks were prepared from unexposed tape coated with polyacrylic resin. In these samples mercury and cadmium were assayed by atomic absorption spectrophotometry.

Mercury was determined by the cold vapour technique on a double-beam monitor for mercury determination, manufactured by the firm of Laboratory Data Control (U.S.A.) and equipped with a mercury lamp, a 30-cm long quartz cuvette and a recorder. The determination limit with this instrument is 0.2 ng of Hg at a wavelength of 254 nm.

Cadmium was determined by the electrothermal atomization technique. The measurements were run on a Beckmann 1272 atomic absorption spectrophotometer equipped with a Massmann graphite cuvette and a deuterium background corrector. Experimental conditions (temperature, time) are given below.

Drying		Combustion		Atomization		Cleaning	
°C	s	°C	s	°C	s	°C	s
120	3	400	30	1800	17	2500	4

Tables 1 and 2 list results of the investigation of concentration distribution of mercury and cadmium in atmospheric aerosol collected on the tape segments A, B and C.

#### 4. MICROMETRIC ANALYSIS

Particles with a size range of 0.01—1  $\mu\text{m}$  were collected on copper microscopic gauzes, 3 mm in diameter, 200 mesh, coated with a  $2 \times 10^{-2}$ - $\mu\text{m}$  thick collodion film or a  $10^{-2}$ - $\mu\text{m}$  thick metallic gold film. The latter was deposited on a collodion backing. The gauzes were then placed in

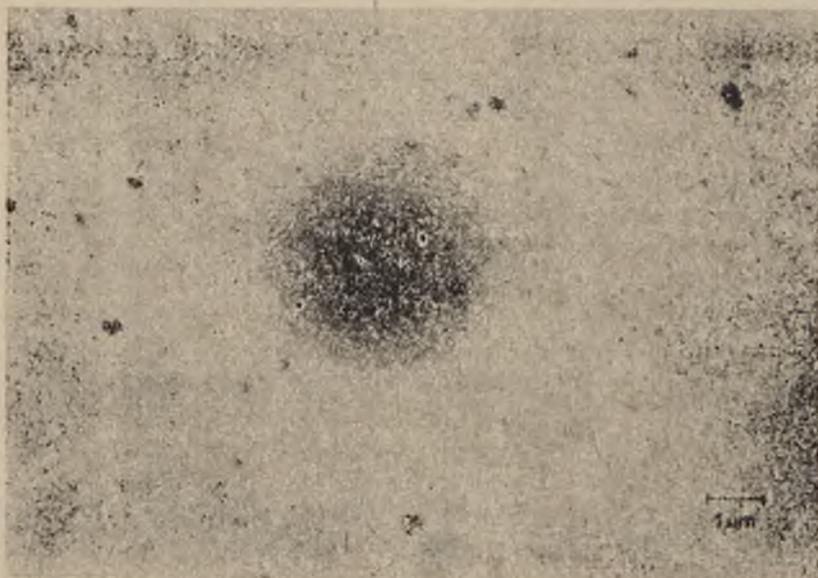


Fig. 3. Microphotograph of the particles of atmospheric aerosol deposited on metallic gold foil, at a 7300-fold magnification.

Rys. 3. Mikrofotografia cząstek aerozolu atmosferycznego na złotej błonie przy 7300-krotnym powiększeniu.



Fig. 4. Microphotograph of standard mercury particles deposited on metallic gold foil at a 7300-fold magnification.

Rys. 4. Mikrofotografia wzorcowych cząstek rtęci na złotej błonce przy 7300-krotnym powiększeniu.

the spiral impactor at a distance of 24, 72 and 120 cm from the air inlet. To collect one sample, about 1000 m<sup>3</sup> of air was passed through the impactor. The samples collected on the gauzes were dried in a desiccator and subjected to dispersimetric analysis under an electron microscope. The particles were photographed (about 60 photographs being taken of one gauze) and analysed by means of a reader (magnification 6.5×) and a viewer (magnification 1.5×; Fig. 3, 4).

## 5. ANALYSIS OF RESULTS

The results of the determination of mercury and cadmium by the atomic absorption spectrophotometric method were compared with the results of the dispersimetric analysis of the aerosol. There were differences (Tables 1 and 2) in the concentrations of mercury and cadmium in samples collected at Gdynia and in the Baltic Sea, within segments A, B and C.

For the Baltic Sea, a maximum for mercury occurs on segment A and for Gdynia in segment C. With cadmium, segment A predominates for both Gdynia and the Baltic Sea.

To examine the relationship between the concentrations of the two metals and the dynamics of submicron particle distribution in greater

Table 1. Concentration of mercury and cadmium in two particle-size intervals of atmospheric aerosol ( $\mu\text{m}$ )  
 Tab. 1. Stężenie rtęci i kadmu w dwóch przedziałach wielkości cząstek aerozolu atmosferycznego ( $\mu\text{m}$ )

Fraction dis- tribution Rozkład frakcji	Gdynia, January '77 — styczeń 1977			Baltic Sea, Apr. '77 — Bałtyk, kwiecień 1977:			
	Conc. of Hg Stężenie Hg ppm	Conc. of Cd Stężenie Cd ppm	ns/Nj	Conc. of Hg Stężenie Hg ppm	Conc. of Cd Stężenie Cd ppm	ns/Nj	
							0.01—0.1
Segment A	107.4	42.4	0.41	$26.8 \times 10^3$	21.5	0.45	0.30
Segment B	14.6	6.5	0.21	$0.2 \times 10^3$	0.9	0.15	0.50
Segment C	792.0	22.9	0.38	$29.5 \times 10^3$	4.7	0.40	0.20

Remark: the results for Gdynia were obtained from an analysis of an aerosol collected from 1181 m<sup>3</sup> of air, those for the Baltic Sea from 1188 m<sup>3</sup> of air.

U w a g a: Dane dla Gdyni uzyskano na podstawie analizy aerozolu zebranego z 1181 m<sup>3</sup> powietrza, dla Bałtyku — 1188 m<sup>3</sup> powietrza.

Table 2. Concentration of mercury and cadmium in two particle-size intervals of atmospheric aerosol ( $\mu\text{m}$ )  
 Tab. 2. Stężenie rtęci i kadmu w dwóch przedziałach wielkości cząstek aerozolu atmosferycznego ( $\mu\text{m}$ )

Fraction dis- tribution Rozkład frakcji	Gdynia, February 1978 — luty 1978			Baltic Sea, February '78 — Bałtyk, luty 1978			
	Conc. of Hg Stężenie Hg ppm	Conc. of Cd Stężenie Cd ppm	ns/Nj	Conc. of Hg Stężenie Hg ppm	Conc. of Cd Stężenie Cd ppm	ns/Nj	
							0.01—0.1 $\mu$
Segment A	63.4	12.4	0.39	273.6	608.2	0.42	0.32
Segment B	52.4	5.1	0.25	15.8	38.8	0.2	0.33
Segment C	134.6	7.8	0.35	112.9	144.2	0.37	0.35

Remark: The results for Gdynia were obtained from an analysis of an aerosol collected from 729.4 m<sup>3</sup> of air, those for the Baltic Sea from 650.59 m<sup>3</sup> of air.

U w a g a: Dane dla Gdyni uzyskano na podstawie analizy aerozolu zebranego z 729,4 m<sup>3</sup> powietrza, dla Bałtyku 650,59 m<sup>3</sup> powietrza.

detail, an analysis was made of the ratio of the number of submicron particles,  $n_s$ , to the total number of submicron particles,  $N_j$ , collected on the surface of the  $j$ -th segment (A, B or C). The values obtained for these ratios conformed with the differences in the mercury and cadmium concentrations found. The highest values of the concentration of mercury and of the  $n_s/N_j$  ratio are indicative of the dominating influence of the particle size range 0.1 — 1  $\mu\text{m}$  in the transfer of this element in Gdynia. In the open sea regions, smaller particles (<0.1  $\mu\text{m}$ ) have a decisive effect. On the other hand, particles with sizes below 0.1  $\mu\text{m}$  contribute most in the transfer of cadmium both at Gdynia, i.e. in the transient zone from land to sea, and in the open sea regions.

The results, on the whole, do not contradict conclusions concerning the contribution of mercury to the aerosol for presubmicron and giant particles [4]. This is seen from a graphic analysis (Fig. 2) of the difference,  $d_r$ , calculated from the equation:

$$d_r = \left( \frac{\sum_{r_i = r_1}^{r_k} n r_i}{N_j} \right)_A - \left( \frac{\sum_{r_i = r_1}^{r_k} n' r_i}{N_j} \right)_B,$$

where  $r_i$  is the  $i$ -th particle radius interval and  $r_k$  is its upper limit to which the sum of particles,  $\sum n r_i$ , is calculated. It follows from the analysis of the contribution of particles and comparison with the results of measurements of mercury content on three segments (Tables 1 and 2) that the contribution of submicron particles determining mercury concentration over marine regions becomes important as from the radius of about 0.07  $\mu\text{m}$  downwards. The contribution of these particles with a radius greater than 0.07  $\mu\text{m}$  clearly declines, attaining a minimum for  $r \approx 0.15 \mu\text{m}$ . For the sake of comparison, the results of an analogous analysis [4] for presubmicron particles are as follows: the contribution of particles becomes important beginning from the radius  $r < 6 \mu\text{m}$  and attains a maximum at  $r \approx 4 \mu\text{m}$ .

For Gdynia, particles with a radius of  $r > 0.05 \mu\text{m}$  contribute within the submicron range, at a maximum for  $r \approx 0.5 \mu\text{m}$ . For the presubmicron particles, however, the range moves to  $r > 6 \mu\text{m}$ .

To sum up the results for the Baltic Sea, the important contribution of particle sizes of two ranges of magnitude,  $r < 0.07 \mu\text{m}$  and  $r \approx 4 \mu\text{m}$  can be noted in the transfer of mercury. Consequently, the contribution in respect of the mass of the particles is almost equal, thus revealing the importance of submicron particles in the transfer of mercury. Similar results were obtained for cadmium, the contribution of particles — car-

riers of cadmium — being almost equal for Gdynia and for the Baltic Sea. Consequently, the method enabled to discern the essential contribution of submicron particles, in particular those with  $r < 0.1 \mu\text{m}$ , in the transfer of mercury and cadmium. It also enabled some differences resulting from comparison of the characteristics of aerosols for Gdynia and for the Baltic Sea to be noted. There is a tendency (Fig. 2) to shift the spectrum of the submicron particle size, the major carriers of mercury, towards larger particles. It seems, however, that the method does not permit an increase in the selectivity of the spectrum of particles by their role in the transfer of mercury.

It would be particularly important for the method to determine the content of the heavy metals in particular particles directly. Such studies were carried out by Bigg and associates [1] and were concerned with the detection of sulphate, ammonium, and chloride ions, as well as sulphuric acid. In this study the method applied consisted in the identification of spots of a chemical reaction occurring between the backing and the aerosol sampled. To do this, metallic gold was vacuum-deposited on to a collodion film placed on the microscopic gauzes. After exposure of the gauzes in the spiral impactor, spots characteristic for gold amalgam were examined using the electron microscopic technique. Around certain spots bright borders appeared after the reaction (Fig. 1). To verify these spots, the metallic gold foil was exposed to mercury vapours and examined (Fig. 2) under an electron microscope to find similar spots. Appearance of the spots depends largely on the thickness and purity of the metallic gold foil. To obtain reproducible results, foil of identical thickness and purity should be used. We used films with a thickness of  $50 \times 10^{-4}$ ,  $70 \times 10^{-4}$  and  $100 \times 10^{-4} \mu\text{m}$ , the best results being obtained with the foil  $70 \times 10^{-4} \mu\text{m}$  thick. Taking into account the finding by Tufts and Lodge [8] that the spot size is linearly related to the content of an element, the next step in our work will be to adopt this method for quantitative measurements.

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## METODA BADAŃ UDZIAŁU METALI CIĘŻKICH W AEROSZLU MORSKIM W ZALEŻNOŚCI OD ROZKŁADU WIELKOŚCI CZĄSTEK

### Streszczenie

W pracy podjęto próbę wyjaśnienia wpływu fizyko-chemicznych charakterystyk układów dyspersyjnych na efektywność procesów dyfuzji i wymiany metali między morzem i atmosferą. W tym celu próby aerozolu zbierano przy pomocy impaktora spiralnego na dwa różne podłoża. Pierwsze stanowiła taśma celulozowa powlekana żywicą poliakrylową, drugie — siateczki mikroskopowe pokryte złotą błoną. W próbkach zebranych na taśmie celulozowej oznaczano zawartość kadmu i rtęci. Do określania zawartości rtęci w poszczególnych cząstkach aerozolu, stosowano test na złotej błonie.

Metody te pozwoliły na badanie jednocześnie fizycznych i chemicznych własności zebranych cząstek. Przeprowadzone badania aerozolu przy pomocy spektrofotometru atomowo-absorpcyjnego Beckmana, dwuzwiązkowego monitora do oznaczania rtęci oraz pomiary dyspersyjometryczne wykazały występowanie w przybrzeżnej strefie morza w Gdyni i nad otwartymi obszarami Bałtyku różnic w rozkładzie stężeń pierwiastków (rtęci i kadmu) związanych z trzema typami rozkładu wielkości cząstek.

Metoda mikroskopii elektronowej pozwoliła zbadać występowanie w atmosferze w rejonie Bałtyku cząstek niemetalonośnych i metalonośnych wykazujących różny stopień zawartości w nich rtęci.

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