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A METHOD TO INVESTIGATE THE DYNAMICS OF THE CONTENT OF METALS IN THE AIRBORNE COMPONENT OF MASS EXCHANGE BETWEEN SEA AND ATMOSPHERE OVER THE BALTIS SEA*

1. INTRODUCTION

The concentration of heavy metals — and indeed of other chemical elements in the airborne particulate matter — beyond any doubt is affected in a different manner by the size distribution of particles. Even the very source of suspensions will substantially decide on the relationship between element concentrations and the dispersive composition of aerosols [5]. Furthermore, these relationships take various forms, depending on the complicated processes that accompany the transport and spreading of particles in the atmosphere. The concentration dynamics of the particular chemical components largely depend on how long the suspensions remain in the atmosphere, which is strictly connected with their dispersive composition. The above explains the fact why, to quote an instance, airborne iodine concentrations are in reverse proportion to the sizes of particulate matter present in atmospheric air [16].

When investigating particle distribution by their sizes, one obviously should reckon with a scatter of results due to different sampling methods and differences in analytical procedure. As often as not insufficient

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amounts of collected sediment will impose restrictions on the results, involving high accuracy and sensitive measurement methods to obtain reliable results. It is therefore essential to take reference measurements, applying alternative methods to determine the chemical composition of suspensions in the atmosphere [3]. Such methodical problems must be solved before we can fill the numerous gaps in our knowledge of mass exchange in the system of atmosphere/sea.

The aim of the present has been to evolve a method to investigate the relationship between size distribution of particles and concentration of aerosol metals, in order to explain the effect of physico-chemical characteristics of dispersive systems on the efficiency of diffusion processes and the exchange of those components between atmosphere and sea. No such researches were attempted in the Baltic area so far, even though they have been commenced in many areas of the World Ocean [6, 16].

2. METHOD

2.1. AEROSOL SAMPLING

A specially-designed impactor, diagramatically presented in Fig. 1, was used to collect aerosol samples within their different size intervals. Particles in the impactor were subjected to the force of inertia and their capture took place by the action of centrifugal force, gradually increasing as the particles moved in a spiral duct. One can assume uniformly distributed small particle adsorption effect only.

A celluloid tape 3.7 cm wide and 150 cm long, was placed in the duct to collect an aerosol sample. The tape was coated with a thin layer of polyacrylic resin before exposure (the resin was developed and supplied by Polycondensation Resins Division of the Industrial Chemistry Institute, Warsaw). This resin was required to satisfy the following conditions:

1. sufficient and stable viscosity, with no apparent determination, due to the flow of large volumes of air above its surface or due to the fluctuations in water content and air temperature typical of the nearwater atmospheric layer in the Baltic area;
2. sufficient homogeneous transparency, indispensible in analyses by the optical and the electron microscope;
3. high degree of purity and chemical homogeneity, necessary to achieve the precision level desired for the determination of microelements;
4. good solubility in organic solvents.

The resin we obtained satisfied the above requirements exceedingly well. It could be dissolved in ethylic acetate or acetone. This was particularly important when developing a method to determine heavy metals according to their neutron activation.

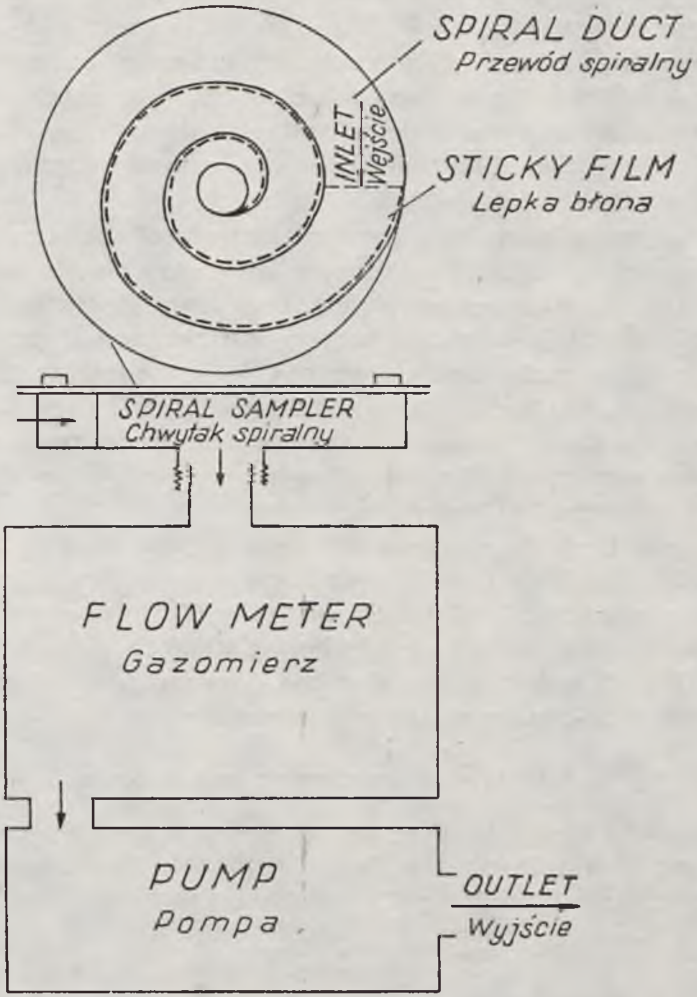

Fig. 1. A sketch of the spiral impactor: spiral chamber outside dia — 33 cm, tape length — 150 cm, intake port — 4 × 11 cm, outlet hole from spiral chamber — 4 × 1 cm

Ryc. 1. Schemat impaktora spiralnego: zewnętrzna średnica komory spiralnej — 33 cm, długość taśmy — 150 cm, otwór wlotowy — 4 × 11 cm, otwór wylotowy w komorze spiralnej — 4 × 1 cm

The spiral impactor was not highly selective in terms of particle separation depending on their dispersive composition. After all, the cascade impactors with a generally lesser throughput of air volume, would not wholly exclude mutual superimposition of spectra of the particle sizes either. We had to reject them, mostly because of excess densification of sediment at each stage of capture, as we wanted to have a chemical and dispersometric analysis at the same time. On the other hand, what the spiral impactor had to offer, was the collection of samples over large areas. Apart from sufficient amounts of sediment to proceed with the neutron activation method, this afforded the possibility to examine the different particles simultaneously, by means of an electron microscope. This method thus enabled us to collect quite substantial samples without the danger of undue densification in the number of particles on the tape surface. Sampling took place at a volumetric pumping rate of air equal to 3000—5000 $cm^3 s^{-1}$.

After a preliminary dispersometric analysis of the samples collected it was decided to divide the exposed tape into three equal segments: 1. segment A — initial section, 48 cm long, counting from the air intake orifice, 2. segment B — middle section, cut between 48 cm and 96 cm distance from the intake, and 3. segment C — or the final section, contained between 96 and 144 cm from the intake orifice. The resin-coated strip on the tape was 2.5 cm wide, while the margins, free of resin, were 0.6 cm wide. Consequently all the collecting surfaces of the segments were equal and amounted to 120 cm^2 per segment.

The optical microscope used for measurements had a magnification rate of 1000. The Tesla type BS 242 E microscope afforded examination of particles magnified 1000 times, up to 30 000 times at the most. The waveforms obtained for the distribution of number of particles for each segment (Fig. 2) demonstrated that the dominant size of particles had a radius of about 1 μm, especially in segment C.

2.2. EFFECTIVITY OF CAPTURE OF PARTICLES

The theory of capture of aerozol particles in aerodynamical appliances has now been elaborated in detail [4, 10, 11]. The movement of particles in a stream of low Reynolds numbers is defined by the formula:

$$\frac{d\vec{v}_i}{dt} = \frac{1}{\tau}(\vec{u}_i - \vec{v}_i) + \frac{\vec{F}_i}{m} \tag{2.1}$$

where $\frac{d\vec{v}_i}{dt}$ — change of particulate matter velocity vector in time, $\vec{u}_i$ — vector of air flow velocity, τ — relaxation time of particle, $\vec{F}_i$ — vector of external forces, m — the mass of particle. By solving equation (2.1) and restricting ourselves to acceleration of gravity forces, we can obtain:

$$\vec{v}_{i+1} = \vec{v}_i + (\vec{u}_i - \vec{v}_i)[[1 - \exp(-\Delta t/\tau)] \tag{2.2}$$

where index i refers to the velocity of the particle towards the capture surface at the beginning of its path; i + 1 — at its end, within the duct segment, Δt — time necessary for the particle to travel along this path.

The effectivity of capture, therefore, can be expressed by

$$\eta = 1 - \exp(-2\vec{v}_{i+1} L/R\vec{u}_i) \tag{2.3}$$

where L — segment length, R — radius of spiral.

In our experiment the air stream velocity was about 0.9 $m.s^{-1}$, at the intake to the spiral chamber, and about 9.5 $m.s^{-1}$ at its outlet. Considering the criterion by N.C. Davies [4], according to which for negligibly small effects of inertia the duct diameter should exceed a value equal to 5 $(Q\tau/4\pi)$, where Q — volumetric velocity of air pumping, we can assert that the parameters of the impactor applied by us were within the sufficient effectivity of particle capture limits. Actually the values for η, in accordance with formula (2.3), even when assuming $(|\vec{v}_{i+1}|/|\vec{u}_i|) = \text{const}$ within the entire duct, could alternate within the following intervals:

Segments	A	B	C
L/R $|\vec{v}_{i+1}|/|\vec{u}_i|$	1.45	2.28	3.84
0	0	0	0
0.001	0.001	0.002	0.004
0.01	0.014	0.021	0.044

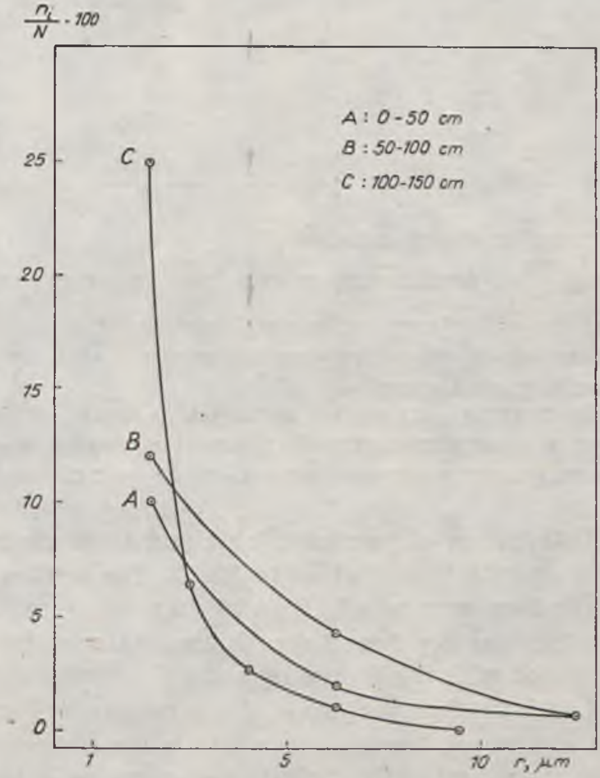

Fig. 2. Probability distribution of particle capture on viscous tape in spiral impactor
A, B, C — successive segments of tape, from the air intake end (distances from intake port are evened up), n_i — number of particles of radius r_i ϑ

Ryc. 2. Rozkład prawdopodobieństwa wychwytu cząstek na lepkiej taśmie w impaktorze spiralnym
A, B, C — kolejne segmenty taśmy od strony wlotu powietrza (odległości od wlotu podane w zaokrągleniu), n_i — liczba cząstek o promieniu r_i ϑ

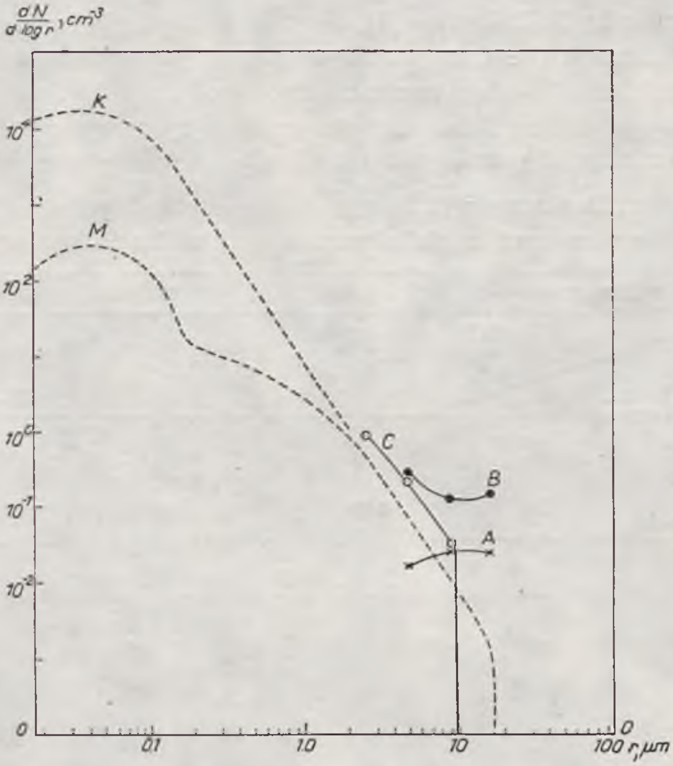

Fig. 3. Size distribution of aerosol particles

A, B, C — values $\frac{dN}{d \log r}$ for the particles collected on successive segments of spiral tape, calculated at an $\eta = 10^{-3}$ cm^{-2} capture efficiency factor

K, M — number of continental and marine aerosols respectively, after C.E. Junge [14]

Ryc. 3. Rozkład liczby cząstek areozolu

A, B, C — wartości dN/d log r dla cząstek zebranych na kolejnych segmentach taśmy spiralnej obliczone przy współczynniku efektywności wychwytu $\eta = 10^{-3}$ cm^{-2}

K, M — liczba cząstek aerozolu kontynentalnego i morskiego wg C.E. Jungego [14]

The size distribution of particles, obtained from measurements for the particular segments, is submitted in Fig. 2. The total number of particles is distributed on segments A, B and C in a 1:4:15 ratio respectively, which is an approximately four times higher rate of capture on each segment as compared with the preceding one.

To proceed with further analysis of the parameters of impactor operation, applied in our investigations, it is worth while comparing the results obtained against the actual size distribution of particles in the atmosphere; such a comparison can be made from the known distribution curves $\frac{dN}{d \log r}$ or the number of particles in relation to the logarithm of their radius, obtained by [14, 15], for the airborne particulate matter above the land and sea respectively. In Fig. 3, data for the impactor are shown in comparison with the distribution curves of particles typical for the atmosphere. The inference is that the collection of particles on segments A and B clearly differs from the distribution series observed in the atmosphere by their size distribution. Again segment C relatively best corresponds to the atmospheric particle size distribution, as if we assume in this case that there is just one value for the factor of capture effectivity for all the intervals of radius r, of a 10^{-3} cm^{-2} order, we obtain a distribution curve resembling the one of the particle size distributions in the atmosphere. Segment A shows the highest values of the number of particle ratio, from the interval of the largest particles versus the number of smallest ones, as shown in Fig. 3, while the lowest values of this ratio coincide with segment C. Consequently the effect of particle distribution, desired to be attained by the experiment, takes a clearly perceptible form in the impactor applied by us.

3. AEROSOL INVESTIGATION BY NEUTRON ACTIVATION METHOD

The method of neutron activation is at present one of the most sensitive methods for the determination of trace metals and other substances in various solvents and adsorbents. The high degree of analytical precision, obtainable with the activation method has also attracted the attention of scientists investigating the problems of transport of microelements in the atmosphere-sea system [6, 16].

In the case of our researches the neutron activation method was particularly preferential in view of the relatively small amounts of airborne particulate matter expected to be collected by means of the spiral impactor above the open sea. To collect sufficiently large suspensions on the spiral tape, thousands of cubic meters of air had to be pumped, while their filtration period had to last for several days. Besides, we had to rely on atmospheric conditions for the success of the experiment while aerosols were sampled. There might be no essential differences in the character of weather when comparing results from remoter time periods. Days free of any precipitation traces, any types of fog or mist were selected to avoid the undesirable effects of additional interference factors on the fluctuations in the concentration of aerosol particles in the near-water atmospheris layer.

Aerosol samples were analysed by the neutron activation method at the Analytical Chemistry Division of the Nuclear Research Institute, Warsaw. To do so, the tape after exposure was cut into segments A, B and C, as above. Blank tests of non-exposed tape, coated and without a coat of polyacrylic resin, were treated simultaneously. Here is an example of such an analysis of aerosol particulate matter, collected during cruises of the „Hydromet" research vessel, specifying a list of data obtained for mercury concentrations:

Item	Type of Sample	Mercury Content (μg)
1.	Resin of non-exposed tape	0.0182
2.	Blank test of non-exposed tape without a resin coat	0.0075
3.	Sediment collected from Segment A surface (0—48 cm)	0.0465
4.	Sediment collected from Segment B surface (48—96 cm)	0.0301
5.	Sediment collected from Segment C surface (96—144 cm)	0.0723

The above data refer to total mercury content per sample. The aerosols collected on polyacrylate resin-coated tapes were hot-washed from them by one to one diluted nitric acid. In view of the anticipated low mercury concentrations in the solutions tested and no possibility of activating large liquid volumes in a reactor, in a high stream of neutrons, a preliminary mercury enrichment was necessary. A new method was evolved preliminarily to enrich mercury present in an aqueous solution, in a freeze-drying (lyophilization) process, in the presence of thioacetic amid-saturated [8] cellulose powder (Whatman 1), used as carrier. The nitric acid sample used for testing was freeze-dried in the presence of about 30 mg of carrier. After weight assessment, part of the carrier was weighed, transferred into a quartz ampule, sealed and subjected to neutron activation, together with a standard reference sample and a blank test (Baltic Sea, Sept., 20—22, 1975).

Resin with absorbed aerosols was also dissolved in acetic ethyl ester. In such cases organic resins (with residue) and acetic ethyl ester were analysed for their mercury contents (Gdynia, April 25 — May 2, 1975). Weighed amounts of resin pieces were sealed in quartz ampules and, together with standard mercury samples, radiated by a thermal neutron stream, of $\Phi = 10^{13}$n cm^{-2} s^{-1}, in an EWA type nuclear reactor, for about 24 hours. Details on mercury determination in samples tested by the neutron activation analytical method were submitted in earlier studies [7, 21].

Table 1 sets out the results of assessing the distribution pattern of total mercury concentrations in the samples. Using particle size distribution, their number and mean density, the concentration in ppm for each sample can be obtained. Data pertain to the near-surface atmospheric layer for the coastal zone of Gdynia and for the open Baltic areas. Aerosols in Gdynia were sampled by the same spiral impactor as at sea, exposing its tape in the nearshore zone at an elevation of about 18 m a.s.l. In the open Baltic, air was pumped from the highest deck of the

Table 1

Tabela 1

Aerosol mercury concentration and the share of giant and presubmicron aerosol particles in its transport above the Baltic Sea

Stężenie rtęci aerozolowej oraz udział w jej przenoszeniu nad Bałtyk cząstek olbrzymich i presubmikronowych

Fraction Distribution Rozkład frakcji	Gdynia, Apr. 25-May 2, 1975 Gdynia 25.04—2.05.1975 r.			Baltic Sea, Sep. 20—22, 1975 Bałtyk 20—22.09.1975 r.		
	Hg concentration (ppm) Stężenie Hg w ppm	n_g $10^2\ cm^{-2}$	$\frac{n_g}{N_j}$	Hg concentration (ppm) Stężenie Hg w ppm	n_p $10^2\ cm^{-2}$	$\frac{n_p}{N_j}$
Segment A (0—48 cm from intake port) (0—48 cm od wlotu)	3.3	60.3	0.66	13.3	30.9	0.34
Segment B (48—96 cm)	11.1	323.9	0.86	0.7	53.7	0.14
Segment C (96—144 cm)	4.0	1018.4	0.77	3.6	304.2	0.23

Data for Gdynia were obtained from an analysis of aerosols collected from a volume of 1125.4 cu. meters of air, for the Baltic — from 1104.5 cu. meters of air.

Dane dla Gdyni uzyskano na podstawie analizy aerozolu zebranego z 1125,4 m^3, dla Bałtyku — 1104,5 m^3 powietrza.

„Hydromet" exposing the spiral impactor from the free air intake side, at a height of about 6 m a.s.l.

The comparisons of data obtained by the neutron activation method with those resulting from dispersion measurements of suspension samples are shown in Table 1. The figures given in the table are, of course, relative. The different particle number and size spectra is mostly responsible for particulate total mass and Hg concentration distribution from segment to segment. In Table 1 there is a conspicuous difference in mercury concentrations assessed for Gdynia and the Baltic Sea within segments A and B respectively. While in Gdynia Segment B predominates over Segment A in respect of mercury concentrations, in the Baltic Sea it is Segment A which prevails. Now this difference cannot be explained away otherwise than by the effect of dispersive properties of aerosol. In this case the divergency cannot be attributed to the magnitude of error only, as the deviations of values obtained exceed all limits of error by far. The measured values were derived from a thorough analysis of samples collected from more than one thousand cubic metres of air per sample. Admittedly, the values thus obtained can be considered as merely approximating the absolute values, nevertheless, the fact that the higher values exceed the lower ones by several times (almost twenty times in the case of the Baltic) has been confirmed beyond any doubt. The most important feature, however, is that those differences between A and B, for Gdynia and the Baltic respectively, are by their sign.

The above difference between the values measured was applied to check the theses assumed at the outset of the present study. To this effect, a dispersometric analysis of the collected aerosol samples was carried out. The total number of particles for the samples collected at sea oscillated around 10^4 cm^{-2} in Segment A, $4 \cdot 10^4$ cm^{-2} in Segment B and $15 \cdot 10^4$ cm^{-2} in Segment C. The total number of particle ratio for segments A:B:C, constitutes in principle a constant parameter of the spiral impactor, and drastic changes in the dispersive composition of suspension would be necessary to alter this parameter. No such changes could de expected under normal atmospheric conditions.

Both the non-homogeneous physical characteristics and in all probability also the complex chemical composition of the particles tested may be decisive for the differences ascertained. There are multiform processes going on in the atmosphere, which, depending on the particles' composition, may result in their growth and chemical changes. To investigate the values obtained from this point of view, several assumptions can be made, as follows:

1. Metals, including mercury, will only join part of the atmospheric dispersive system,

2. Mercury can be absorbed by all particles, in amounts proportionate to their mass,

3. Only mercury vapour or its compounds can be adsorbed, and this process is restricted to the outer surfaces of aerosol particles.

The first assumption seems to be motivated true. It was checked by us by means of a newly-developed unique method, according to which a distinction is made between metal-bearing and submicronic or presubmicronic non-metal-bearing particles. This was achieved by means of an electron microscope and a report is furnished below.

To adopt the second assumption, one should expect a correlation to exist between the total mass of particles present in the suspension and Hg concentrations in the particular segments. The mass of particles on segments A, B and C in our experiment corresponded to a 1:8:7 ratio accordingly. Therein the minimum values of the sum of the mass of particles, connected with segment A, contradict the highest mercury concentration recorded in this segment over the Baltic. If we further examine the distribution of the total volume of particles in connection with their size spectra (Fig. 4), we shall ultimately conclude that the second assumption is not fully compatible and therefore it may not furnish a sound basis to explain the mercury concentration differences in obtained difference in the mass of suspensions.

To adopt the third assumption, the total surface area of particle distribution was analysed, depending on sizes (Fig. 5). Still, as will be

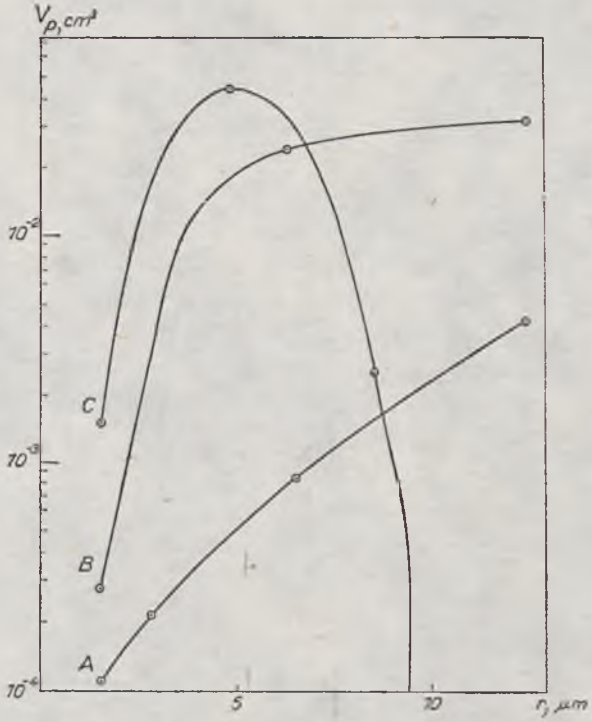

Fig. 4. Summaric volume of particle distribution, depending on their different dispersive composition in the successive segments, A, B, C of the spiral tape

Ryc. 4. Rozkład sumarycznej objętości cząstek w zależności od różnic ich składu dyspersyjnego w kolejnych segmentach (A, B, C) taśmy spiralnej

seen when comparing Figs. 4 and 5, the distribution of the total surface of particles, within the interval of magnitudes of particle radius r tested does not, in principle, deviate much from the character of mass distribution for identical segments, A, B and C; such being the case, there is also no justification for the differences in mercury distributions in Gdynia and above the Baltic when comparing the particle surfaces against their mass ratio. Hence the conclusion is that the third assumption cannot fully hold true.

The above assessments ultimately necessitated that we concentrate our attention on the first assumption again. If not all the particles have metal-bearing qualities, the differences in metal concentrations in atmospheric aerosols must obviously take place in close connection with the dynamics of particle size distribution. Taking this as the starting point, the ratio of the number of presubmicronic sizes (n_p), and of giant sizes ($n_g = N_j - n_p$) to N_j — total number of particles collected on the surface of j-th Segment (A, B or C) was examined. It was then found that the values obtained for those ratios do not conflict with the assessed differences of mercury concentrations in air; on the contrary, they agree with

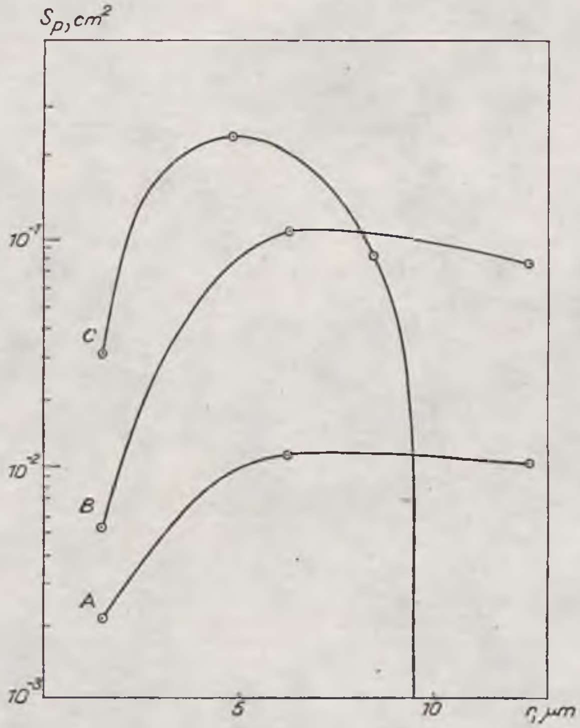

Fig. 5 Summaric surface area distribution for collected particles depending on their different dispersive composition in the successive segments, A, B, C of the spiral tape

Ryc. 5. Rozkład wielkości powierzchni sumarycznej zebranych cząstek w zależności od różnic składu dyspersyjnego w kolejnych segmentach (A, B, C) taśmy spiralnej

these (Table 1). Thus, following these investigations, we arrived at a confirmation of the evident correlation occurring between the dynamics of the dispersive composition of aerosol in the atmosphere and concentrations, in this instance of mercury, which are airborne with the suspension.

Highest values of mercury concentration and $\frac{n_g}{N_J}$ ratio, reported for Gdynia, bear witness of the predominant importance of giant particles in the transport of this element in the transition zone between land and town areas on the one hand and the sea on the other. Again, above the open Baltic waters, a prominent rôle in this respect is played by particles far more minute. The residence time of the giant particles in the near-water atmospheric layer is round one day on average [12]. The self-purification process consequently is rather intense and hence the differences assessed for Gdynia and open Baltic areas respectively, referring to the values of n_g/N_J and e_p/N_J ratios and in the mercury concentrations connected therewith.

Let us now attempt to define the difference of variation between $(n_p/N_j)_A$ and $(n_p/N_j)_B$, gradually as the reach of n_p is shifted towards ever larger particles. As we know

$$\frac{n_p}{N_j} = 1 - \frac{n_g}{N_j} = \frac{\sum\limits_{r_i=r_1}^{r_k} n_{r_i}}{N_j} \tag{3.1}$$

where: r_i — the successive, i-th interval range of particle radius magnitude, r — its upper limit of magnitude, to which the sum of particles, $\Sigma\, n_{r_i}$ is calculated. In accordance with the above, the difference, d_r, is defined from the equation:

$$d_r = \left(\frac{\sum\limits_{r_i=r_1}^{r_k} n_{r_i}}{N_j}\right)_A - \left(\frac{\sum\limits_{r_i=r_1}^{r_k} n_{r_i}}{N_j}\right)_B \tag{3.2}$$

The diagram obtained for d_r in its r_i function (Fig. 6) indicates that the share of particles that can affect mercury concentrations above the sea areas, starts to be accountable, from the range of radii below 6 μm.

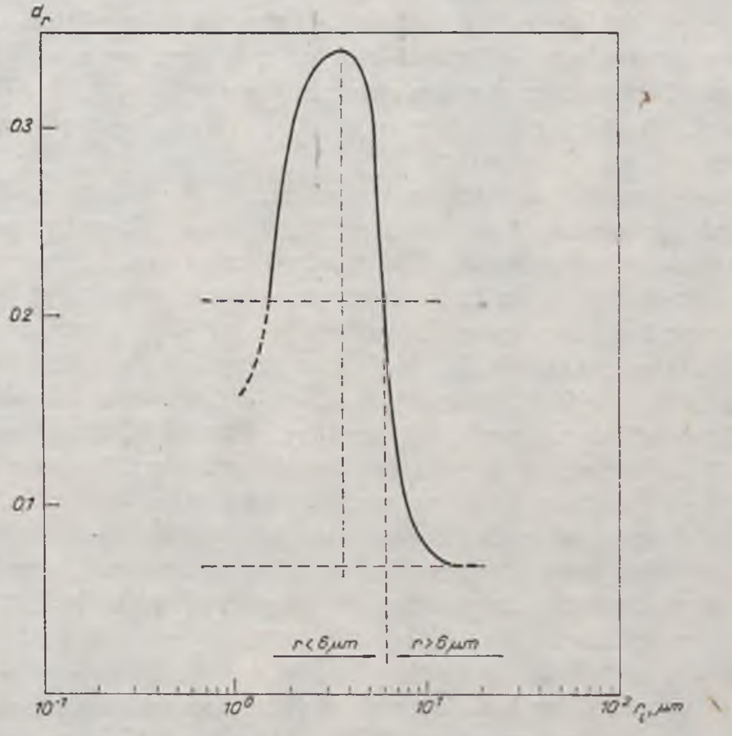

Fig. 6. Function d_r value distribution, by size of atmospheric aerosol particles in the Baltic Sea area

Ryc. 6. Rozkład wartości funkcji d_r według wielkości cząstek aerozolu atmosferycznego w rejonie Bałtyku towards the smaller particles. Maximum value is already achieved after radii of 4 μm are exceeded. Again, the curve declination towards submicron particles for the present must be treated with caution, as this is to some extent the effect of the method applied in particle sampling and dispersometric analysis. This interval will necessitate further analyses to be carried out by means of an electron microscope. Further, the range of particle sizes which, according to Table 1, is responsible for mercury transport in the Gdynia coastal zone, is determined in Fig. 6 by a curve section around the lower extremum of d_r, and corresponds to the particle range of $r > 6$ μm.

4. ELECTRON MICROSCOPE INVESTIGATION OF METAL-BEARING PARTICLES

As mentioned above and demonstrated in Fig. 3, according to C.W. Junge [15] we may conclude that the dominating sizes of atmospheric aerosol particles fall within the range of radii of 10^{-2} — 10^{-1} μm. These particles, in spite of their numbers, amount to lesser total mass than does the multitude of presubmicron size particles, not to mention the giant ones. Still, assuming that not all the particles within their respective size intervals are of metal-bearing qualities, we are faced with the problem of submicron particle share in the mechanism of airborne metal transport. First of all, however, a check must be made whether this presumption is right or wrong.

It is possible to analyse the chemical composition of the single particles by means of an electron microscope. The rudiments of this method are simple indeed. The method consists in bringing a known chemical reaction down to microscopic size and observing the course of reaction and effects by electron microscopy. Many authors have proposed different methods for such investigations. In principle, all these ideas consist in affording conditions, in which ions react at the interfaces, where two solutions meet, followed by removal of the solvent [2, 17—20]. The microscope is used to observe and identify the characteristic products of reaction. Still, no such method may be applied to analyze single airborne particles because the introduction and subsequent removal of liquid reagents from the solution at the same time may change the natural chemical composition of the particles themselves.

A genuine method to detect the presence of sulphate, chloride and ammonia ions as well as sulphuric acid in submicron size aerosol particles was proposed by E.K. Bigg et al. [1]. It consists in vacuum spraying of a suitable reagent on nitrocellulose films for subsequent identification of typical stains of chemical reaction, which will be seen after aerosol particles are deposited on the film thus treated. Basing on the idea suggested by E.K. Bigg et al., we propose the present unique method of determining the content of transient and heavy metals content in the single aerosol particles. The method consists in the application of the ditizone test.

4.1. THE METHOD

Copper microscope grids 3 mm in dia. and total mesh of 200, were used to collect aerosol samples. A collodion film, 200 Å in thickness, was applied. After numerous preliminary trals, a collodion film made up of 1 per cent collodion solution in n-amyl-acetate wac found the best, and most resistant to the stream of electrons (after previous treatment with an air stream), and sufficiently permeable for the electron stream. The grids thus prepared were placed on small glass plates and subjected to an air stream in a one-cascade impactor. About 10 cubic meters of air were passed through the impactor at a rate of 0.15 cbm/min to collect one sample. Aerosol samples were exsiccated in a dehydrator and tested under Tesla type BS 242 E electron microscope, with a magnification of about 1000—30 000.

To run the test, a nitrocellulose ditizone-saturated film was prepared. Ditizone was selected from among the reagents bearing affinity to metallic ions because it forms stabile crystalline complexes with the majority of transient and heavy metals, to the latter of which mercury belongs. Ditizone will also dissolve in n-amyl acetate. A number of ditizone solutions in a 1 per cent collodion solution was made, from which to prepare films of different ditizone content. The most appropriate film, assumed by trial and error to be resistant to the action of an electron stream after exposure in an air stream, and sufficiently permeable to the stream of electrons, also yielding clear reaction traces, is the one obtained from 1 per cent collodion and 50 per cent ditizone solution in n-amyl acetate. The ditizone-collodion film thus obtained was deposited on the microscope grid surfaces. To protect the film from direct with metallic copper, being the material of which grids are made, the grids were first coated with a very fine film of collodion (a 0.5 per cent collodion solution). Also all precautions were taken to avoid direct contact of the ditizone-collodion film with metals, during all manipulations.

4.2. METAL-BEARING AND NON — METAL-BEARING PARTICLES IN THE ATMOSPHERE

In the course of testing atmospheric aerosol samples by the method described above, photos of particles were taken, from which the metal-bearing ones were clearly distinguishable from those which would not carry any metals. Actually in micro-photographs 1 through 4, distinctly visible dark ringlets made their appearance around some of the particles.

Photo 1. A micro-photograph of airborne aerosol particles on a ditizone-collodion film — a magnification of 9.600

Fot. 1. Mikrofotografia cząstek aerozolu atmosferycznego na błonie ditizonowo-kolodiumowej przy 9600-krotnym powiększeniu

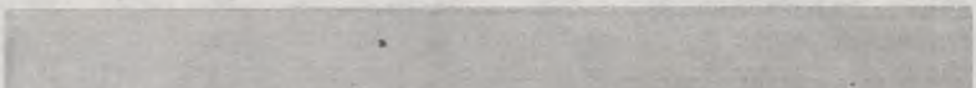

Photo 2. A micro-photograph of airborne aerosol particles — a magnification of 30.000

Fot. 2. Mikrofotografia cząstek aerozolu atmosferycznego na błonie ditizonowo-kolodiumowej przy 30 000-krotnym powiększeniu

Photo 3. A micro-photograph of airborne aerosol particles on a ditizone-collodion film — a magnification of 9.600

Fot. 3. Mikrofotografia cząstek aerozolu atmosferycznego na błonie ditizonowo-kolodiumowej przy 9600-krotnym powiększeniu

Photo 4. A micro-photograph of airborne aerosol particles on a ditizone-collodion film — a magnification of 15.200

Fot. 4. Mikrofotografia cząstek aerozolu na błonie ditizonowo-kolodiumowej przy 15 200-krotnym powiększeniu

Judging by the results of our tentative experiments with metallic grids, condusted to verify this effect, the traces appear to be due to a chemical reaction taking place between ditizone and the metal ions.

It should be stressed here that the dark ringlets differ in their intensity. So we can observe some particles yielding very dark and distinct reaction traces (Phot. 1), while others have their ringlets weak and obscured, hardly perceptible. Those traces will often not be seen at all unless under very high magnification (Photos 3 and 4). Apart from the clearly visible reaction traces, some particles did not show any reaction at all (Photos 1 and 2). It appears, then, that if we are to develop this method, we shall be able not only to assess the presence of metal ions in particles, but also to determine the amounts of metals in the particular aerosol fragments. To this effect we can rely on the previously ascertained fact, according to which the magnitude of reaction trace making its appearance under the conditions described above, more or less approximates the linear function of quantity of the element tested [18].

The microphotographs obtained in this study pertain to particles of aerosol collected in the longshore area of the sea in Gdynia. In the course of testing, aerosol samples collected above the open Baltic Sea waters were also examined. The results obtained confirm the assumption that-apart from the metal-bearing — non-metal-bearing particles are also present in the near-water atmospheric layer. This assessment refers both to the submicron and presubmicron sized particles.

5. CONCLUSIONS

1. The method of atmospheric aerosol sampling applied in our investigations, i.e. the passing of large air volumes through a spiral impactor, is adequate for simultaneous examination of both physical and chemical properties of the samples collected. This method, enabling samples of suspensions, large enough to be analysed by the neutron activation method, to be collected, also enabled us to carry out measurements of dispersive characteristics of aerosol particles, using the optical and the electron microscope.

2. Aerosol investigations by means of neutron activation to determine mercury concentrations and by particle dispersion measurements, revealed considerable discrepancies in the distribution patterns of mercury concentrations, connected with three types of particle distribution by their sizes in the nearshore sea area in Gdynia and above the open Baltic waters respectively.

3. The differences in mercury concentration distributions, obtained for the coastal sea in Gdynia and the open Baltic areas, find their

justification in the relationship assessed in the course of this research project between mercury concentrations in atmospheric aerosols and the count ratio of the number of presubmicron and giant particles to the total number of particles present. In the coastal zone, mercury concentrations rise mainly to the component of giant particles, while above the open Baltic a similar effect is occasioned by the component of substantially lesser particles, their sizes verging on the submicron size interval.

4. The above assessment is an argument to support the pertinence of the proposal to use the self-purification constaant Λ — of a magnitude determined for the near-water atmospheric layer from the investigations of sea salt nuclei above the Baltic [12] — when calculating the extent of the mercury transport (fallout) stream passing into the sea from the atmosphere, in the case of the Gulf of Gdańsk [13].

5. The statement concerning the effect of the number of particles from different size intervals on atmospheric mercury concentrations is correct and in accordance with the presence of metal-bearing, as well as non-metal-bearing particles in the atmospheric aerosol composition. While developing a unique method to trace and test metal-bearing particles with the use of an electron microscope, we obtained confirmation by experiment of the presumption that both metal-bearing and non-metal-bearing particles, the former showing different metal concentrations, occur in the atmosphere in the Baltic Sea and nearshore areas.

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METODA BADAŃ DYNAMIKI UDZIAŁU METALI W AEROZOLOWEJ SKŁADOWEJ WYMIANY MASY MIĘDZY MORZEM A ATMOSFERĄ NA BAŁTYKU

STRESZCZENIE

Zastosowano metodę pobierania prób aerozolu atmosferycznego z dużych objętości powietrza z użyciem do tego celu impaktora spiralnego. Próby zawiesin zbierano w ilościach dostatecznie dużych dla dokonania ich analiz metodą aktywacji neutronowej. Przy pomocy mikroskopu optycznego i elektronowego przeprowadzono jednocześnie analizę charakterystyk dyspersyjnych zawiesin. Opracowując oryginalną metodę badania cząstek metalonośnych z zastosowaniem mikroskopu elektronowego potwierdzono eksperymentalnie występowanie w atmosferze w rejonie Bałtyku cząstek niemetalonośnych obok cząstek metalonośnych, wykazujących różny stopień zawartości w nich metali. Na przykładzie różnic w stężeniu rtęci, pokazano, że w strefie przybrzeżnej na wzrost stężenia rtęci w atmosferze wpływa głównie składowa cząstek olbrzymich, podczas gdy na otwartym Bałtyku — składowa cząstek wielkości presubmikronowych.

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