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THE ANALYSIS OF THE ANIONS CONTENT IN PRECIPITATED WATER BY THE METHOD OF ISOTACHOPHORESIS IN THE AREAS OF SIEDLCE AND OLECKO

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COMMUNICATION

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Abstract: This paper presents the results of the research aiming at determining content of selected anions in the samples containing precipitated water (rainwater and snowfall water) by isotachophoretic method. This work is a continuation of the complex pollution monitoring in the areas of Siedlce and Olecko (near Suwałki). The samples were collected from November 2006 to May 2007. Days of sampling depended on atmospheric conditions. Sulfate and hydrogen carbonate turned up to be the dominant anions in samples which were collected in city centers. Higher contents were observed in Siedlce. The content of nitrites in both cities was low. The highest concentration of sulfates and chlorides in rainwater was obtained in the samples collected near the Company of Thermal Energy (CTE) in Siedlce. Similar results of sulfate concentration were observed in Olecko. In samples of snowfall water (collected near to the CTE) sulfates and sulfites were the dominating anions.

INTRODUCTION

The rapid development of economy, industry, transport and the increase of population do more and more irreversible harm to the environment. Air, water and food are basic and the most important substances for the living organisms. Their quality influences people's health.

Water is the most widespread chemical compound on the earth and the most basic element which enables the existence. It is irreplaceable and vital for the proper performance of all organisms (respiration, temperature regulation, assimilation of alimentary substances). The daily water consumption of a human being should be between 1.5 to 3.0 dm^3, depending on many other factors, e.g. temperature, kind of the job performed, climate, and the body mass. However, drinking water does not fulfill standards and is polluted. It transfers diseases which can be dangerous [7, 11, 18, 19],

Precipitated water comprises significantly less minerals than river, lake and underground water. Its components depend mainly on the composition of the atmosphere. The components of air are among others: dust and gases issued by volcano eruptions, ashes

from burning wood or aerosols derived from chemical reactions of gases emitted during decomposition of organic substances. On the other hand, anthropogenic sources of air pollution are processes of solid, liquid and gaseous fuel burning (power stations, heat and power generating plants, an individual house heating and transportation). Impurities are also emitted by the chemical industry (refineries, through the production of chemical fertilizers), the waste storages and come from agriculture (spraying fertilizers and plant protection agents) [6].

The atmosphere is chemically a very complex system. Many natural chemical reactions take place there, but some human activities interfere with the balance of these processes, mainly when compounds, alien to the environment, form an unnatural composition. In these cases, as the results of chemical reactions show it, some new compounds are synthesized and fall down on the earth. They penetrate surface water and spread through rain, snow, dew and precipitation [18].

Presently, human economic activity is considered to be the dominant source of air contamination. Industrial activities were not controlled for many years and their negative influence on the environment was not considered as harmful. The basic factor for economical development is the energy. We still process energy by burning coal, mainly brown coal and products originated from petroleum, natural gas and turf. Significant increase of pollution is observed in winter, because of stronger emissions of burning products during the season of household heating. This effect, first of all, can be observed in places with big number of low, dispersed emitters (chimneys of one-family houses or boiler houses). Coal and petroleum burning causes big problems for the environment, because numerous chemical compounds are spread to the atmosphere then [7, 18].

The second factor with significant influence on the air quality is transport. Continuous augmentation of car number causes worry over the composition of the air, which is inhaled by us. Contamination emitted into the air as the products of fuel burning causes directly or indirectly a threat to our health. Despite the production of more and more new fuels, which show decreased content of toxic constituents, despite the construction of new sparing engines, immense number of vehicles causes contamination of the atmosphere [18].

Combustion gases' emission is the main source of carbon oxide, which reacts with hemoglobin impairing blood circulation. The next substance found in gases is carbon dioxide, the most "famous" greenhouse gas. Then – nitrogen oxides, which irritate and damage respiratory passages and dust, which irritates higher respiratory passages and contains toxic heavy metals [19].

Therefore, it is necessary that the air and water are protected against contamination and consequently, there is need to conduct adequate investigation.

EXPERIMENTS

The investigation concerns the analysis of water (from rainfalls and snowfalls) collected in the areas of two cities (Siedlce and Olecko). The number of inhabitants in Siedlce is four times higher than the one in Olecko; the distance between the cities is 255 km. Both cities are insufficiently industrialized. They were chosen to be the examples proving a correlation between population and the anions content in precipitated water. Samples of snowfalls (after melting) are of the volume of 2 dm^3 and were collected in December

2006, January and February 2007. Rainfall samples were collected in December 2006, March and May 2007. Exact dates of collection depended on weather conditions.

The places of collection were chosen due to the location of the sources of environmental pollution (intensive traffic and coal burning by the Company of Thermal Energy). Collected samples were stabilized by the addition of EDTA, in order to inhibit catalytic oxidation of nitrite and sulfite ions. These ions in the presence of oxidants are oxidized to nitrates and sulfates. The analysis of ions content for nitrates, nitrites, chlorides, sulfites, sulfates and hydro carbonates was carried out by isotachophoresis method. The first step was the preparation of solutions and standard curves for particular ions. Then, the collected samples were divided into 2 sets – to undergo a qualitative or a quantitative isotachophoretic analysis. The spectrophotometric analysis of the chosen samples had been performed before and showed differences under 5%.

REAGENTS AND APPARATUS

During the investigation, the following reagents were used (all analytically pure): the leading electrolyte LE-1 for a preseparational column, prepared from equal volumes of the following solutions: NaCl solution (POCh Gliwice, $8 \cdot 10^{-3}$ mol/dm^3), 1,3-bis[tris(hydroxyethyl)methylamino]propane solution (Aldrich, $3 \cdot 10^{-3}$ mole/dm^3), β-alanine solution (Aldrich, $1.5 \cdot 10^{-3}$ mol/dm^3), hydroxyethylcellulose solution (Aldrich, 0.1%);

- the leading electrolyte LE-2 for an analytic column, prepared from equal volumes of the following solutions: NaCl solution ($2 \cdot 10^{-3}$ mol/dm^3), β-alanine solution ($1.5 \cdot 10^{-3}$ mol/dm^3), hydroxyethylcellulose solution (HEC), (0.1%);
- terminating electrolyte TE: citric acid (POCh Gliwice, $5 \cdot 10^{-3}$ mol/dm^3);
- deionized water for preparation of standard solutions (Merck);
- sodium chloride (POCH Gliwice);
- sodium sulfate (POCH Gliwice);
- sodium sulfite (POCH Gliwice);
- sodium nitrate (POCH Gliwice);
- sodium nitrite (POCH Gliwice);
- sodium hydrocarbonate (POCH Gliwice);
- EDTA (POCH Gliwice).

The analyses were carried out by means of a isotachophoresis analysator EA 202M produced by Villa Labeco s.r.o. in Spisska Nova Ves equipped in: preseparation column (diameter 0.8 mm, length 90 mm), analytic column (diameter 0.3 mm, length 160 mm) conductometric detector for every columns with a measurement range between 20 kΩ and 30 MΩ.

The samples (volume $3 \cdot 10^{-5}$ dm^3) were inserted in the separation system by a feeding valve. The data reported by the detectors were then transformed in a personal computer equipped in the special program ITP Pro 32 (KasComp, Bratislava, Slovakia).

The isotachophoretic method of anion determination was subjected to the validation according to some generally accepted principles [2, 3, 8, 9, 13]. The method performed was examined by determining such parameters as: recovery, precision, the limit of identification and linearity.

RESULTS AND DISCUSSION

Table 1 shows the profile of used analytical method with some data concerning qualitative and quantitative analyses. The elaborated method is characterized by a high precision (under 5%) and wide range of linearity (1–30).

Table 1. Characteristic of used analytical method

Parameter	Unit	For examined ion
Precision[1]	%	2.3–3.3
Recovery[2]	%	91.5 ± 6
Linearity[3]	mg/dm^3	1–30
Limit of identification[4]	mg/dm^3	1

[1] – n = 4, the samples were analyzed twice;
[2] – the sample was enriched with 1.5 cm^3 of a solution containing 1 mg/cm^3 of examined ion, n = 4;
[3] – correlation coefficient above 0.98;
[4] – calculated from the limit of identification and coefficients of the calibration curve.

The average results are shown in Tables 2–5. The water protection against the contamination is a very important task for our economy. The prevention of water pollution means the limitation, omission and elimination of a contamination, and in particular, the contamination of substances outstandingly harmful to the environment. The human activity has led to the degradation of hydrosphere in many places. Due to this unpredictable action, the protection of the environment has become a real necessity, because the balance between the amount of produced contaminants and natural possibility of regeneration had been disturbed.

Table 2. Average content of individual ions [μg/dm^3] in samples of rainfall collected in the town centre

Anion	Siedlce			Olecko		
	Month					
	December	March	May	December	March	May
NO_3^-	13.3	13.9	15.1	14.2	14.7	14.3
NO_2^-	7.6	14.1	6.2	8.3	10.7	7.5
HCO_3^-	45.2	60.1	53.2	39.1	47.2	46.8
SO_4^{2-}	64.2	69.3	48.6	50.1	58.3	57.4
Cl^-	33.2	38.4	36.1	30.4	36.2	37.9
SO_3^{2-}	21. 8	20.9	13.7	15.6	17.2	13.3

Table 3. Average content of individual ions [μg/dm^3] in samples of snowfall collected in the town centre

Anion	Siedlce			Olecko		
	Month					
	December	January	February	December	January	February
NO_3^-	16.6	18.1	17.9	15.0	16.2	16.9
NO_2^-	9.2	13.4	13.0	7.9	13.6	12.1
HCO_3^-	41.2	47.6	30.8	38.2	44.6	44.1
SO_4^{2-}	56.7	62.1	58.9	49.9	53.7	48.6
Cl^-	23.4	27.1	26.8	20.8	21.1	24.3
SO_3^{2-}	12.1	13.9	11.6	11.0	14.3	12.5

Table 4. Average content of individual ions [μg/dm³] in samples of rainfall collected near the heat and power plant

Anion	Siedlce			Olecko		
	Month					
	December	March	May	December	March	May
NO_3^-	19.2	19.9	17.3	18.4	19.2	15.7
NO_2^-	12.2	12.4	7.1	11.0	10.7	4.3
HCO_3^-	30.1	37.8	35.6	22.1	28.3	28.4
SO_4^{2-}	61.3	63.4	45.1	54.2	56.8	52.9
Cl^-	36.9	41.5	40.3	21.1	26.2	23.4
SO_3^{2-}	26.9	38.6	25.4	24.7	33.9	32.6

Table 5. Average content of individual ions [μg/dm³] in samples of snowfall collected near the heat and power plant

Anion	Siedlce			Olecko		
	Month					
	December	January	February	December	January	February
NO_3^-	22.2	24.6	24.8	18.9	19.2	19.3
NO_2^-	17.3	14.2	15.1	7.9	10.3	9.5
HCO_3^-	28.6	34.9	33.7	24.5	29.8	34.2
SO_4^{2-}	60.6	62.1	63.4	41.5	44.9	43.7
Cl^-	33.6	35.9	35.2	21.8	24.6	25.2
SO_3^{2-}	41.2	44.8	37.6	30.1	28.9	29.6

The preventive methods of water pollution are complex; i.e. as contamination comes from different areas of human activity. This attitude enables us to avoid a significant loss, which, if we do not start any preventive actions, will be impossible to stop. It concerns the human health, the disappearance of some species of plants and animals and landscape degradation.

The liquidation of polluted water is very expensive; therefore, a prevention of contamination is much more economical and thus better. It can only be done by legal prohibition of bringing wastes [16], sewage [12] from contaminated areas, toxic chemical substances and other materials into the water as they are incredibly harmful. Also, washing cars by means of the surface water, spreading agricultural sprayers directly over plants and mixing it together with the source of water, as well as the use of organic compounds (of tin for conservation of underwater construction) should be prohibited [14].

Water is the most important compound affecting a quality of any human life. Therefore, prevention, as well as the legally regulated protection is necessary. Up to now, some acts concerning the protection of water in Poland have been edited [12, 14, 15, 17].

Both towns, Siedlce and Olecko, are situated in the areas which are still insufficiently industrialized. Olecko is situated in the region of the so-called "Green Lungs of Poland", however, relatively intensive and still increasing traffic as well as different systems of heating local households is serious sources of contamination. Olecko has 17000 inhabitants; its area is of the 1142 ha. The commune of Olecko belongs to the most frigid zones of Poland (the average vegetation time is 185–195 days, snow cover remains 70–100 days, average water precipitate is 550–750 mm/m²). The increasing number of tourists and transit traffic through the area of this town, as well as its neighborhood cause increase of contamination by dust and heavy metals.

Similarly, Siedlce is situated in a transient climate zone. An average summer temperature is between 12.2°C and 23.9°C. In winter, it is respectively, -4°C and 1.2°C. An average water precipitation is 522 mm/m^2, the population – 76279 inhabitants, the area's surface – 3187 ha.

Samples of rainfall and snowfall were collected in the centre of the town, where the intensity of vehicle traffic was the highest and the places were in the vicinity of heating and power generating plants. It is commonly known that cars and side-products of petrol derivatives, coal, wastes etc. emit significant amounts of contaminants to the atmosphere. The atmospheric contaminants are diffused at different distances, and then fall onto the ground (along with precipitation) and cause degradation of soils and some surface waters. Rainwater is often analyzed for heavy metals; however, the content of anions is omitted [7].

The investigations of precipitated water and simultaneous investigations of atmospheric contamination are important for many reasons. Surface waters, which are supplied by water precipitation, are utilized for alimentary, economic and industrial reasons. Research, which allows for predicting future menaces and trends, is desirable.

As Tables 2–5 shows, the quality of air in the "tested" towns depends on the traffic as well as heating production and power plants, which emit great amount of contaminants. In the samples of snowfall water collected in the centre of towns, the highest concentration of sulfates – 62.1 μg/dm^3 was observed in Siedlce in January 2007, the lowest in Olecko in February 2007 – 48.6 μg/dm^3 (Tab. 3). In the samples of rainfall water, in the centers of towns, the highest concentration of sulfates was reported in Siedlce in March 2007 – 69.3 μg/dm^3, in Olecko – 58.3 μg/dm^3 (Tab. 2). However, the highest concentrations of sulfates were observed in the samples of rainwater collected near the heat and power plant (in Siedlce – 63.4 μg/dm^3 and in Olecko 56.8 μg/dm^3). Similar results are shown by the samples of snowfall collected in both cities near the heat and power plant. It confirms the earlier results obtained by some other authors [1, 4, 5, 10].

The sources of contamination summarized above may progressively aggravate the quality of life of the inhabitants in Olecko and Siedlce. The air purity in the region of Olecko is described as one of he best in Poland. But the increasing intensity of the traffic becomes a threat for the present atmospheric, naturalistic and acoustic conditions. A slight influence of contaminants on the atmospheric quality can already be observed.

A little higher contamination is shown by the results obtained from the samples collected in Siedlce, but the purity of the atmosphere in this city is still satisfactory. It is connected with the agricultural function of this region. The highest (at about 60%) rate of emission of contaminants belongs to professional energetic sources. The participation of the town traffic in the emission of contaminants is also significant (20%). Because of the increasing number of vehicles in the area, this factor will become more and more harmful, particularly in the centre of the town. In the majority of little plants and service stations, which throughout their professional activity emit various contaminants to the atmosphere (mainly dusts and gases), some positive changes appeared; new, and quite modern technologies were applied. The emission of contaminants caused by household heating systems is also onerous; however, it generates exceedingly and causes too high concentrations of some toxic substances on a limited area and causes local pollution.

CONCLUSION

The presence of the examined ions in water precipitation (rainfalls and snowfalls) in the areas of Siedlce and Olecko, shows a significant influence of the heating and power plants and cars on the degree of contamination of the atmosphere. The investigation proves a correlation between the content of examined anions in water precipitation and the intensity of derivatives from burning petrol and natural gas by the heating and power plants. The low contents obtained in the analyzed samples, prove the slight atmospheric contamination in the areas of the towns discussed above. Due to an insufficient industrialization, the expected increase of contamination in the future will rather be low.

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ANALIZA ZAWARTOŚCI ANIONÓW W WODACH OPADOWYCH MIAST SIEDLCE I OLECKO TECHNIKĄ IZOTACHOFOREZY

W pracy przedstawiono wyniki analizy zawartości wybranych jonów w próbkach wód opadowych (deszczu i śniegu) metodą izotachoforezy. Praca jest kontynuacją kompleksowego monitoringu zanieczyszczeń miast: Siedlce i Olecko koło Suwałk. Próbki zbierano od listopada 2006 r. do maja 2007 r. Ze względu na występowanie opadów termin zbierania poszczególnych próbek uzależniony był od warunków atmosferycznych. W próbkach pobranych z centrum badanych miast dominującymi anionami okazały się siarczany(VI) i wodorowęglany(IV). Wyższe zawartości badanych anionów stwierdzano zawsze w mieście Siedlce. W obu miastach stwierdzono najniższe zawartości azotanów(III). Z kolei w próbkach deszczu pobranych w pobliżu Przedsiębiorstwa Energetyki Cieplnej w Siedlcach odnotowano najwyższe zawartości siarczanów(VI) i chlorków, a w Olecku – siarczanów(VI) i siarczanów(IV). Natomiast w próbkach śniegu pobranych obok PEC w obu miastach dominującymi anionami okazały się siarczany(VI) i siarczany(IV).