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THE TEMPERATURE DEPENDENCE OF THE PH-SENSITIVE GLASS ELECTRODES

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The elimination of temperature influence on the glass electrodes is important in the application of potentiometry to environmental analysis, where the monitoring is carried out in the different temperature conditions.

The temperature dependence of the glass electrodes at the range of temperatures 0 - 40 °C was studied. The potentiometric cell, such as Ag/AgCl, buffer | glass | test solution, KCl bridge, Hg/Hg₂Cl₂ was used. The pH values of the buffer solutions inside the glass electrodes were chosen 1.68, 4.01, 6.86 and the experiments were carried out in the solutions at pH values 1.68, 4.01, 6.86, 9.18 and 12.45.

At the constant temperature, the pH response of the electrode system is given in the form of Nernst equation: $E = E^{\circ} - k\text{pH}$, where slope factor k theoretically is equal to $2.3 RT/F$, E° is the standard potential of the cell including a number of factors controlled by the experimental conditions, notably the concentrations of the inner and external electrolytes and there is an assumption liquid-junction potential being constant.

The potential dependence on the pH of 8 glass electrodes by the 3 different inner solutions and 5 test solutions was examined. The differences of the glass electrode potentials did not overcome $\pm 2\text{mV}$ at the same test solution. E , pH dependencies were stable in time. The slope factors were in the range of 53 - 62 mV/pH unit and varied linearly with temperature, in accordance to the theoretical Nernst slope factor $\partial k/\partial T = 2.3 R/F$ [1]. The values of the isopotentials do not coincide with the values of the pH of the inner electrolyte solutions. The difference was 0.5 - 2 pH units, which is based on the asymmetry of the glass electrode.

Table 1. Temperature dependence of the resistance ($g\Omega$) of pH-sensitive glass electrode.

t, °C Nr. of the electrode	0.9	5.2	10.0	14.9	20.0	25.0	30.0	35.0	40.0
1	1.509	1.075	0.720	0.428	0.244	0.163	0.100	0.078	0.055
2	1.760	1.403	1.003	0.623	0.333	0.211	0.109	0.096	0.062
3	1.920	1.388	0.816	0.509	0.360	0.216	0.102	0.082	0.058
4	1.850	1.285	0.835	0.563	0.322	0.167	0.099	0.088	0.075
5	1.540	1.136	0.722	0.444	0.274	0.147	0.093	0.062	0.055
6	1.960	1.445	0.894	0.592	0.364	0.223	0.121	0.101	0.083
7	2.080	1.720	1.222	0.743	0.341	0.135	0.092	0.084	0.062
8	2.110	1.780	1.270	0.845	0.296	0.188	0.123	0.090	0.048

The potentials of the inner and external reference electrodes were measured also separately in the 0.1 M KCl solution. On the bases of the measured potential values the asymmetry potentials for the glass electrodes in the range of 3 - 25 mV were calculated. The values of the asymmetry potential were different at the different inner solution. The above mentioned differences are similar to the literature data [2].

The resistance of the glass membrane was measured by shunting the cell and the values of the resistance were calculated from the change of the output signal of the cell. The resistance of the glass electrodes are given in Table 1.

As it seen from the Table 1 the resistance of the glass is essentially increasing near to the temperature $t = 0\text{ }^{\circ}\text{C}$. The temperature dependence on the glass resistance quite well coincides with the data given in literature at the temperature over $10\text{ }^{\circ}\text{C}$, but the discrepancies increase at the temperatures near to $0\text{ }^{\circ}\text{C}$ [3].

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CONCENTRATION AND SPECIATION OF TRACE METALS IN THE GOTLAND DEEP

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Introduction

In 1993/94, very large volumes of saline waters intruded the Baltic Sea from the North Sea. This caused, following a stagnation period of almost 15 years, *inter alia* a sudden redox turnover in the bottom water of the central deep basins. In the Eastern Gotland Basin, oxygen levels not observed since the 1930's, replaced the highest H₂S concentrations never recorded before in the Baltic Sea. In the Gotland Deep, the concentration and speciation (particulate, colloidal, anionic and cationic forms) of trace metals (Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn) has been investigated in the water column before (1991) and after (1994) the salt water inflow.

Rationale

A rough estimate of metals imports from the North Sea was made. Assuming typical North Sea (Norwegian Trench) metal concentration, with 100 km³ water around 280 t Fe, 80 t Mn, 25 t Ni, 20 t Cu, 3 t Pb, 2 t Cd and 0.3 t of Hg have been imported in "dissolved" (<0.4 µm) form. However, inflow events may create much more important effects than simply their import with the inflowing water masses. Two scenarios could reflect this:

Scenario A: Allow the change from anoxic to oxic conditions to occur for 50 % of the deeper parts (>150 m) of the Gotland Basin. This would affect about 3300 km² of sediment surface. With (a) an average sedimentation rate of 1 mm/yr, (b) deposits with 0.1 g dry material cm⁻³

containing 2 - 10 $\mu\text{g Cd g}^{-1}$, of (c) a 1 cm thick layer of surface sediments shall be affected by the oxidation of sulphidic Cd forms. By this oxidation, 6.6 - 33 t Cd could be released into the bottom water in a relatively short time span. The uniform distribution of this Cd in the Gotland Basin below 150 m (110 km³) would add about 60 - 300 ng l⁻¹. Distributed solely in an 1 m thick bottom layer, the concentration would increase therein to 2 - 10 $\mu\text{g Cd l}^{-1}$, or about 200 times higher than normal concentration of dissolved Cd in Baltic waters!

Scenario B: Major water inflow events cause significant redox-mediated changes for other metals, i.e. the concentrations of the dissolved Fe, Mn and Co certainly decrease by orders of magnitude. In the eastern Gotland Basin, an anoxic water mass of ca. 304 km³ existed under pre-inflow conditions, extending from about 125 m down to the bottom (~240 m). A decrease of the dissolved iron concentration from ca. 90 $\mu\text{g l}^{-1}$ to 0.5 $\mu\text{g l}^{-1}$ under oxic conditions would have resulted in the precipitation of more than 27000 t Fe. For manganese, a change in the dissolved concentration from 400 $\mu\text{g l}^{-1}$ to 2 estimated $\mu\text{g l}^{-1}$ would produce more than 120000 t particulate Mn. For the trace element Co, a drop of the dissolved forms from 50 ng l⁻¹ to about 5 ng l⁻¹ means that almost 14 t of Co may have been precipitated within a few weeks. Freshly precipitated manganese but also iron oxihydroxides are very efficient collectors for trace metals. Consequently, some metals may have been very efficiently coprecipitated and finally deposited.

Experimental

(A) In May 1991 and in August 1994, sampling were performed from r/v *A. v. Humboldt* at the HELCOM/BMP station. The samples were pressure filtered and acidified to pH<2, and solvent extracted within the next few days. The metals were analysed by flame injection and flameless (GF)AAS:

(B1) Sampling for trace metal speciation studies was performed at station F-81 on 29 June 1994 from r/v "Aranda". 10 samples were taken, 6 were from the previously strongly anoxic water layer below 200 m. On-line filtration under nitrogen of ca. 4 l water performed using 142 mm/0.4 μm PORETICS polycarbonate filters. To release the particulate metals, the loaded filters were leached several weeks with 2 M HCL/1 M HNO₃.

Two liter each of the filtered sample were used for the extraction of different metal and organic species, respectively. The extraction of

metals followed an approach used by LEWIS & LANDING (1992) for studies in anoxic Black Sea waters. Under nitrogen, the samples passed consecutively 3 columns, the first for the separation of colloids, the second one for the removal of polyanionic dissolved humic substances and of other anionic including hydrosulphide complexes, and the third one contained a cation exchange resin based on immobilized 8-hydroquinoline. For metal elution, 2 M HCl/1 M HNO₃ was passed through each of the single columns. The leachates from the filter treatment and the eluates from the columns were directly used for metal determination by flame injection (Fe, Mn, Zn) and/or flameless (GF) AAS (Cd, Cu, Fe, Mn, Mo, Ni, Pb, Zn).

(B2) To separate potential chelators, the filtered samples passed columns retaining colloids (see above) and a consecutive set of C8- and C18-*SepPak* type materials. The columns were eluted consecutively with 4 ml each of different water/acetonitrile (ACN) mixtures. The initial (30 %) eluates from the first two columns, representing colloidal and dissolved organic material, respectively, were analyzed on their Cu and Ni content by (GF)AAS.

Results

Changes in total dissolved trace metal concentrations, 1994 vs. 1991

The results of the measurements show that in 1991 metals like Mn, Fe and Co increase from very low concentration in the surface layer to respectively >500, >50 and >20 times higher levels below 125 m. Because Mn is released from the bottom sediments and not precipitated, it increases continuously downwards. For Co and Fe however, maximum concentrations appear at 150 m and 200 m, respectively. Thereafter, their dissolved forms may be controlled by sulphide precipitation. In the hydrogen sulphide containing water, Cd, Cu and Zn decrease to about one tenth of their respective concentrations at 50 m. Pb and Ni decrease below 125 m by about 25 %. However, below 200 m Cd and Pb, and below 225 m Cu and Zn as well, increase significantly toward the bottom. This may be due to the mobilization of these metals in the presence of higher H₂S concentrations as sulphide complexes, as well as the enrichment of sulphidic colloids, which are recorded as "dissolved" forms, above the sediment.

In 1994, the vertical concentration profiles of the investigated metals have drastically changed against their pre-inflow patterns, both

qualitatively and quantitatively. Below 120 m, dissolved Fe, Mn and Co concentrations dropped very low levels whereas the concentrations of Zn, Cu and Cd increased significantly. Ni is now evenly distributed over the water column. At 140 m, the Pb profile depicts a pronounced minimum (0.4 ng l^{-1}), approaching concentrations close to 30 ng l^{-1} above and below that depth. In August 1994, at 120 m an oxygen minimum with only 0.02 ml l^{-1} persisted. In this samples, still typically pre-inflow conditions were met, i.e. comparatively high dissolved Mn ($150 \text{ } \mu\text{g l}^{-1}$), Fe ($8.5 \text{ } \mu\text{g l}^{-1}$) and Co concentrations (34 ng l^{-1}), and the lowest value for Cd (7 ng l^{-1}) and Cu ($0.24 \text{ } \mu\text{g l}^{-1}$).

Metal speciation under post-inflow conditions

Below 200 m, practically the total concentration of Mn ("total" used here as sum of all measured fractions) exists in particulate form. Close to the sediment, almost $200 \text{ } \mu\text{g Mn}_{\text{part}} \text{ l}^{-1}$ were observed, i.e. the same order of magnitude as Mn_{diss} in 1991 under pre-inflow conditions ($> 400 \text{ } \mu\text{g l}^{-1}$). In 10 m and 50 m depth, the Mn concentrations were $< 2 \text{ } \mu\text{g l}^{-1}$, mainly in dissolved cation forms. In the halocline (70 m) and at 125 m, between 14 and $18 \text{ } \mu\text{g Mn}_{\text{cat}} \text{ l}^{-1}$ were measured. At the previous interface between oxic and anoxic conditions (125 m), almost identical concentrations of dissolved and particulate fractions were met.

Down to the sea bottom, except for the 10 m sample, the speciation of iron is dominated by the particulate forms. However, related to the pre-inflow dissolved Fe concentrations in bottom water, in June 1994 only about 10 % were recovered as particulates. This behaviour differs significantly from that of manganese (see above) and may be due to the much faster re-oxidation and setting kinetics of Fe. In all samples, a low but rather constant concentration of cationic iron ($< 0.5 \text{ } \mu\text{g l}^{-1}$) was found. The anionic forms are even lower, i.e. close to the detection limit. In nearly all samples, the colloidal Fe concentration was higher than the total ionic fraction, but still below $1 \text{ } \mu\text{g l}^{-1}$. In the euphotic layer, the colloidal iron represented the main fraction (ca. $2 \text{ } \mu\text{g l}^{-1}$), possibly due to organic associates arising from the primary production.

In the speciation of zinc, the cationic fraction with concentration around $2 \text{ } \mu\text{g l}^{-1}$ dominates. With a maximum in 236 m, except for a depth of 50 m, appreciable amounts of zinc are also present in particulate forms. Anionic and colloidal Zn appear with concentrations $< 0.5 \text{ } \mu\text{g l}^{-1}$.

Colloidal zinc shows higher concentrations in the halocline and at 220 m, anionic forms have their maximum in the euphotic layer.

The Mo geochemistry seems to resemble that of the Mn.

The particulate Cu represents between 10 % and 30 % of the total concentrations which range between about 200 and 450 ng l⁻¹. For most samples, the colloidal fraction is much lower than the particulate one, but still in significant amounts, except for the 50 m depth. Below 200 m, within the truly dissolved Cu fraction, the cationic forms dominate. An exception is the extraordinary Cu-rich sample at the oxygen minimum layer in 220 m. The "excess copper" found at that depth is mainly due to anionic forms. This could reflect remains from Cu complexes, which may have "survived" in the relict waters still showing very low oxygen concentrations. In the samples between 10 m and 125 m, the percentages of the cationic and anionic forms are nearly identical.

For nickel, the cationic forms dominate. The variations with depth are low. Colloidal and anionic forms are close to the detection limit. The same holds true for "organic colloidal nickel" eluted with 30 % ACN. Particulate Ni appears in the order of 5 - 10 % of the "total" concentrations (400 - 500 ng l⁻¹). Related to the total dissolved concentration, the organic species, separated with C8-*SepPak* and eluted by 30 % ACN, seems to occur in much lower percentages than the corresponding Cu forms.

In most of the samples, the speciation of lead is dominated by the cationic forms, closely followed by the particulate fraction. Below 210 m, with the exception for 230 m, the colloidal fraction reaches a significant level and even dominates in the 220 m and 236 samples. As for copper, there is a much higher lead concentration at 220 m than in the adjacent water layers.

For cadmium, the cationic forms clearly dominate. The percentage of the anionic species is much lower, often almost negligible. As for Zn, below 200 m the particulate fraction of cadmium becomes significant and increases toward the bottom.

ADVANCES IN GAS CHROMATOGRAPHIC DETERMINATION OF AIR POLLUTANTS

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From 1960's gas chromatography has become one of the main methods for determination of toxic chemical compounds in atmosphere and workplace air. Improvement of chromatographic methods for separation of impurities, working out of selective and high-sensitive systems of detection and development of reactive gas chromatography (RGC) have made it possible to increase selectivity of chromatographic methods, reduce detection limits (DL) for many toxic substances and improve the identification of components in complex mixtures of air pollutants in recent 10 years.

Working out a technology for preparing reproducible highly effective thermostable capillary columns with immobilized stationary phases, use of selective stationary phases and also improvement of preparation technology of capillary columns with a thin layer of adsorbent at the inner surface of capillary tube (PLOT-columns) enabled to make and manufacture chromatographic columns for separation of almost any kind of mixtures of organic volatile compounds and inorganic gases.

Development of element-selective microwave and radiofrequency plasma detectors, improvement of construction of chemoluminescence-, flame ionization- (FID) and flame photometrical (FPD) detectors, working out new types of electron capture detectors (ECD) and utilization of principles of reactive gas chromatographic detection form the bases for significant improvement of analytical methods.

The main problems of analytical chemistry of air contaminants is the extraction of toxic substances from air and reliable identification of target components in complex mixtures of contaminants continue to be actual. These problems are closely connected to each other: selective

separation of individual contaminants or classes of chemical substances makes significantly easier their following detection and increases its reliability.

The most popular methods of trapping of air pollutants which are based on the use of traditional solid sorbents (activated charcoal, silica gel, porous polymers, graphitized carbon blacks, molecular sieves and others) are usually not selective, but after adsorption of pollutants and their extraction from sorbent bed, practically all the peaks of toxic substances present in sampled air can be seen in chromatograms. The latter fact makes the identification of components more difficult and problematic.

It is possible to solve the problem of reliable identification of target components by the means of traditional methods or their combinations with each other and pure chromatographic methods based on the use of retention indexes - GC/MS, GC/Fourier-IR spectroscopy, selective detectors and reactive gas chromatography (RGC). In recent years different variants of RGC are more often used due to their simplicity and effectiveness.

Trapping of impurities from polluted air by chemisorption is based on the formation of derivatives or unstable complex compounds as a result of interaction of air contaminants with sampling material. This method is very highly selective and for reliable identification of target components the chromatographic determination of individual components is sufficient in this case.

Effectiveness of trapping air contaminants by this method lies between 80 - 100 %, the use of ionization detectors reduces detection limit down to the level of 0.0001 mg/m^3 (Table 1). After chemisorptive concentration of carboxyl acids their concentration can be determined directly or in the form of fluorine derivatives obtained in the result of reaction with pentafluorobenzylbromide. In this case detection limit may be reduced 10 - 100 times while detecting with ECD compared to a method using FID.

Formation of unstable mercaptides, easily decomposable by 25 % HCl, in reaction with salts of heavy metals makes it possible to trap selectively microcontents of mercaptanes, sulfides, other sulfur-containing compounds from air and determine them at the level of TLV. Not less effective is a reactive chromatographic determination of aldehydes after their chemisorptive trapping from the air in the form of dimedone, pentafluorobenzylloxime or 2,4-dinitrophenylhydrazine. Use

of thermionic detector (TID) or ECD decreases detection limit down to picogram level.

After chemisorptive concentration of microamounts of nicotine it can be determined directly by TID at the level of 0.0002 mg/m^3 . For the detection of low concentrations of formaldehyde in the air, chemisorption is followed by conversion of it into oxazolidine derivatives that are registered with FID.

In addition to compounds listed in Table 1, there are at least 50 more substances, for which chemisorption methods of concentration are used. Reliability of identification of components while using these kind of methods is guaranteed by selectivity of adsorptive materials.

Preparation of volatile organic derivatives, possible for most organic compounds and inorganic gases, enables realization of not less reliable way of identification of target components than chemisorptive trapping of contaminants. Derivatives can be obtained directly in a sampling bed containing chemisorbent for the enrichment of the sample, but also after sampling contaminants by using traditional sorbents and their desorption by subsequent extraction. Applications of the latter method are significantly broader due to possibility to use various selective reactions of organic chemistry (there are at least 100 - 150 usable reactions). High level of enrichment of the sample allows to determine most of contaminants (Table 2) at ppb level.

Method of determination of contaminants in the form of their organic derivatives has great opportunities for their reliable identification due to the possibility of choosing a suitable "personal" chemical reagent practically for any kind of individual compound, especially for reactive organic substances (aldehydes, ketones, alcohols, acids, amines, etc.) and inorganic gases (nitrogen and sulfur oxides, ozone, hydrides, halogenes, etc.).

Application of reactive-sorption concentration (RSC) of impurities enables to identify target components in complex mixtures with higher reliability compared to traditional gas chromatographic methods like using retention indexes.

Method of RSC consists of intentional removal of disturbing additives (at the time of trapping the contaminants from the air) in a pre-column containing sorbents and chemical reagents and subsequent concentration of target components in a sorbent trap. Fractionation of air sample beforehand with guaranteed recovery of controlled components increases the reliability of identification of compounds 30 - 40 %

compared to traditional chromatographic methods and reduces the error of determination.

For example the method of determination of aromatic hydrocarbons in city air by RSC can be brought. Precolumn with hydroxylamine, acidified with hydrogen chloride and boric acid, removes aldehydes, ketones and alcohols from the mixture and makes it significantly easier to identify accurately target components. At the determination of vinyl chloride in workplace air (production of synthetic leather from polyvinylchloride) it is easy to identify this compound in the chromatogram after removal of many additives present in precolumn containing zeolite 5A, sulfuric acid on glass fibres and Versamide 900. Determination of tetraethyllead in air is less complicated after removal of ozone (precolumn with iron sulfate). The same kind of precolumn is used also for the removal of peroxyacetylnitrates at the determination of nitrogen oxides.

Application of RSC enables to identify reliably carboxylic acids, carbonyl compounds, phenols, styrene, amines, alcohols, sulfur- and halogene-containing organic compounds and many inorganic gases. This method can be used for identification of main classes of organic compounds in complex mixtures of air and water contaminants and for systematical analysis of contaminating substances in different combinations.

Reactive-chromatographic detection (RCD) consists in obtaining derivatives by using selective and high-sensitive detector. This combination enables to determine many essential contaminants in the air at TLV level with high reliability. For illustration of this method a new technology of detection by ECD using RCD may be brought. After chromatographic separation of sulfur-containing odorants (hydrogen sulfide, carbonyl sulfide, carbon disulfide, sulfur dioxide, sulfides, mercaptanes, etc.) they were fluorinated in the flow of fluorine up to hexafluorinated sulfur in a reactor located in a thermostate of chromatograph. Hexafluorinated sulfur was detected by ECD at the level of femtograms. Sensitivity of this kind of detection system is about 100 times higher than in the case of using FPD.

The amount of effective applications of RCD for detection of air contaminants continuously increases. It can be explained by high effectiveness of combination of chemical reactions and chromatographic separation of toxic substances, simplicity and low cost of RCD methods and possibility of realization of this method at almost every laboratory.

Table 1. Chemisorptional trapping of air impurities.

Target components	Sorbent	Detector	Concentration determined mg/m ³
Aldehydes	Amberlite XAD-2 or glass beads covered with 2,4-dinitrophenylhydrazine and phosphoric acid	ECD	0.0001
Aldehydes	20 % solution of NaHSO ₃ on silica gel	FID	10 µg
Formaldehyde	XAD-2 treated with 2-(hydroxymethyl)-piperidine	FID	0.03
	Chromosorb 102 treated with N-benzyl-ethanolamine	FID	0.01
	2,4-dinitrophenylhydrazine on the filter	ECD	0.005
Ethylenoxide	24 % HBr on Amborsorb XE-347	ECD	0.5
Ammonia, aliphatic amines	sulfuric acid on silica gel	TID	0.02 pg
	phosphoric acid on Sep-PAK	FID	0.2
C ₁ - C ₄	0.2 % tartaric acid on glass beads	FID	0.2
Ammonia	Porasil B treated with 5 % KOH	FID*	0.5 ng
Nicotine	NaHSO ₃ on glass fibre filter	TID	0.0002
Monoethanol-amine	cyclohexanone on XAD-4	TID	1 µg
Carboxylic acids	1 % NaOH or Sr(OH) ₂ on glass beads	FID	0.01
C ₁ - C ₅			
Mercaptanes, sulfides	mercury(2+) salts on silica gel	FPD	10 ⁻⁴ - 10 ⁻⁸
Nitrogen dioxide	20 % triethanolamine on glass beads	FID	0.1
Phosphine	silver nitrate on silica gel	FPD	0.001
Stibine	mercury chloride on silica gel	FID	0.01
Hydrogen cyanide	activated charcoal, impregnated with Na ₂ Cr ₂ O ₇ and copper (2+) salts	TID	0.001
dicyane			
Cyclopentadiene	maleic anhydride on Chromosorb P	FID	0.01

* flame thermionic detector

Table 2. Obtaining of derivatives after concentration of impurities in a sorbent bed.

Target components	Derivatives	Detector	Detection limit mg/m ³
Aldehydes	hydrazones	FID, ECD	0.001
	hexamethylenetetramine	FID	0.01
	alcohols	FID	0.1
Acroleine	XAD-2 treated with 2-(hydroxymethyl)piperidine	TID	0.0001
Formaldehyde	methanol	FID	0.01
Alcohols	alcyated nitrates	ECD	0.6 ppb
Carboxylic acids	trimethylsilylethers	FID	0.5 ppb
	anilides	TID	1 µg
	methylethers	FID	0.01
Organic acids, alcohols, phenols	fluorinated products of silylization	FID	0.005
Pentachlorophenols	acetates	FID, ECD	0.005
	ethers	ECD, FID	0.0001
	triethylsulfone complex	ECD	0.0001
Polychlorinated biphenyls and substances similar to them	catalytical dechlorination to hydrocarbons	FID	0.5 µg
Styrene	dibromide	ECD	0.01
Acrylonitrile	bromocyanogen	ECD	0.02
Pesticides	reaction products with hepta fluorobutyric anhydride	ECD, TID	1pg
Hydrazine, methylhydrazines	?	TID	1 ppb
Amines	amides of heptafluorobutyric anhydride	ECD	1 pg
Nitroderivatives of polyaromatic hydrocarbons (diesel exhausts)	catalytical conversion into pentafluoropropylamides	FID, ECD, TID	1 ppb
Dimethylsulfate	acetonitrile	TID	0.5 µg

Continued:

Target components	Derivatives	Detector	Detection limit mg/m ³
Cyanates	trifluoroacetyl derivatives of toluyldiamines or amides of heptafluorobutyric acid	ECD, TID	0.0001
Hydrogen cyananide	pentafluorobenzylcyanide	ECD	0.4 ng
Nicotine	alcylated derivatives	FID	0.01

AROMA COMPOSITION IN THE QUALITY CONTROL OF SARDINES

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Introduction

The flavour of fish products depends on the species and the conditions used for processing and storage [1-6]. More than 280 volatiles have been identified in fresh and processed fish [7]. In fundamental papers by Josephson et al. [1-3] freshwater and saltwater fish aroma compounds were investigated. The results show that carbonyl compounds and alcohols with 6, 8 and 9 carbon atoms are involved in fish flavour [1-6]. They are formed by lipoxigenase-initiated peroxidation on n-3, n-4, n-5 and n-6 polyunsaturated fatty acid and via cleavage of prostaglandins [6, 8, 9]. In comparison with freshwater fish the saltwater fishes have more aroma compounds especially carbonyl containing substances.

Salted and canned sardines are a popular meal in Russia. Early qualitative composition of aroma compounds of fried and boiled sardine was investigated [10]. Alkanals C3 - C11, aliphatic alcohols C3 - C8, cyclopentanol, some n-alkanes, benzaldehyde, all methyl-, propyl- and butylamines were found. But there were no quantitative data on aroma compounds of fried and boiled sardines. Qualitative and quantitative composition of raw, salted and canned sardine volatiles was also not studied.

Our investigation has been carried out (i) to obtain additional information on volatiles of sardine (*Sardinops melanosticta*), (ii) to quantify the levels of flavour compounds and (iii) to study their changes in raw, salted (preserves), boiled and canned sardines processed from one batch of fish.

Experimental

The sardine (*Sardinops melanosticta*) was harvested in Atlantic Ocean and frozen. After two weeks of storage at -18 °C the sardines were processed. At the Kaliningrad Fish Institute (AtlantNIRO) the flesh samples for investigation were obtained from:

- A - raw sardines;
- B - salted sardines processed as preserves;
- C - boiled sardines
- D - canned sardines without addition of oil.

For analyses 1 kg of each sample was taken. The isolation of volatiles from A, B, C, D samples was carried out by codistillation method with diethyl ether [11]. Before isolation procedure 500 µg of n-tridecane was added to the samples as internal standard.

GC analyses were performed on a Hewlett Packard model 5710A and Mega 5300 (Carlo Erba) chromatographs on two fused silica columns with SE-30 (50 m × 30 mm, d = 0.25 µm) and CW 20M (50 m × 0.30 mm, d = 0.25 µm). The column oven temperature was programmed from 50 °C to 220 °C at a rate of 4K/min. The peaks were detected simultaneously with FID and FPD specific to sulphur containing compounds, or FID and ATD specific to N-containing compounds.

GC-MS analyses were carried out with EI by using a Finnigan-MAT model 45151 equipped with a fused silica capillary column SPB-1 (60 m × 0.32 mm, d = 0.25µm). The temperature of analyses was programmed from 40 °C to 280 °C at a rate of 4K/min.

Results and discussion

Volatiles of the aroma concentrate were identified using retention indices on two columns and mass-spectra. For quantitative estimation of volatiles by GC the internal standard n-tridecane was used. As an example, chromatograms of aroma compounds of canned and salted sardine are given on Figure 1.

Chromatogram of N-containing compounds is shown on the bottom of Figure 1, where pyrazine has the main peak. Sniffing analysis effluent on SE-30 column allows to develop three fractions with index interval 850 - 870, 920 - 960 and 1010 - 1060 i.u. They have a fish-like odour in combination with green, cucumber, and fatty notes. It was found that qualitative composition of investigated sample volatiles were different. In raw sardine (A) 19 compounds were identified, in salted

sample (B) - 41, in boiled sample (C) - 45 and in canned sample (D) - 49 substances.

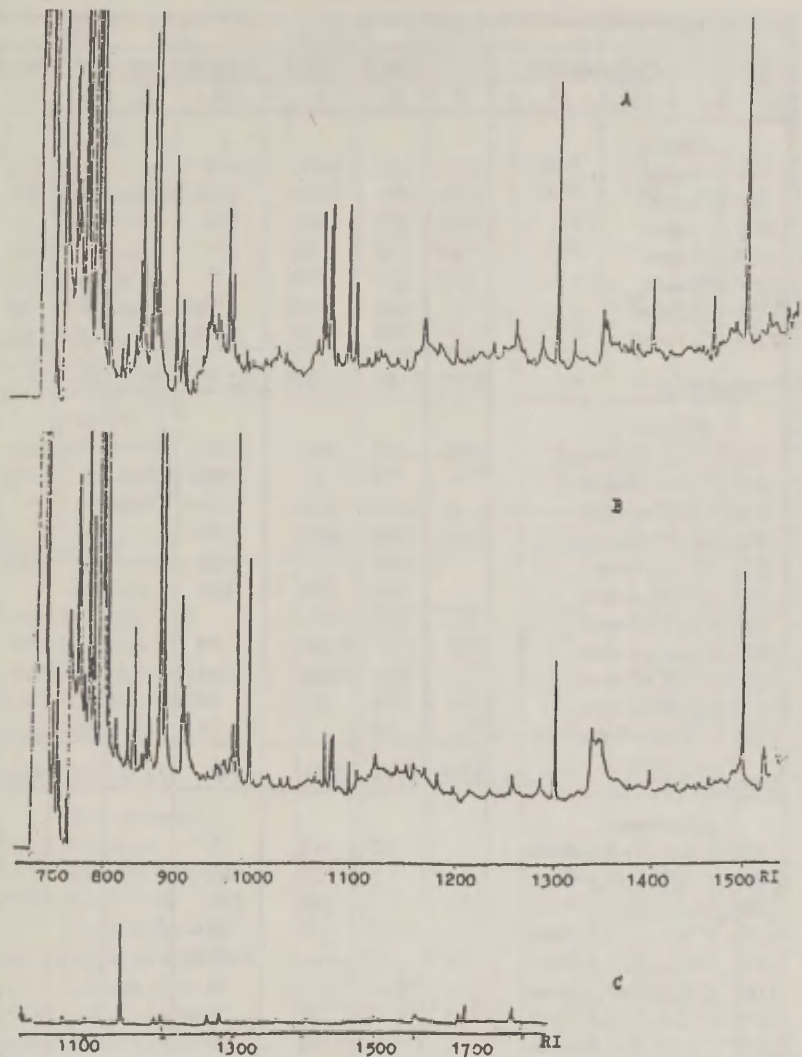


Figure 1. Chromatograms of volatiles from salted (A) and canned (B) sardines on SE-30 and N-containing compounds of canned sardines on CW20.

Table 1. Concentration ($\mu\text{g}/\text{kg}$) of volatile substances found in sardines.

RI	Compound	Sardine				Fishes*		
		raw	salted	boiled	canned	raw	raw	boiled
		A	B	C	D	(3)	(1)	(5)
<i>Alkanals</i>								
679	C5-anal	4750	825	8000	12500	20	-	-
780	C6-anal	1550	3350	3400	1100	418	20.5	37
882	C7-anal	150	450	500	300	16.3	1.8	-
980	C8-anal	10	340	60	290	-	0.6	+
1080	C9-anal	115	220	250	175	10.3	3.2	-
1180	C10-anal	-	20	50	100	-	2.6	-
1284	C11-anal	-	40	25	100	-	-	-
Total ($\mu\text{g}/\text{kg}$)		6575	5245	122285	14565	464.6	28.7	37
<i>Alkenals</i>								
718	3-Me-C4-2-enal	1000	100	200	1050	-	-	-
852	2-Me-C5-2-enal	-	75	75	25	10.9	2	-
794	C6-(Z)-2-enal	2	250	250	300	6.3	-	-
830	C6-(E)-2-enal	-	300	200	150	-	1.4	-
870	C7-(Z)-4-enal	-	50	5	25	-	-	2.8
932	C7-(E)-2-enal	-	200	150	100	-	-	-
990	C8-(Z)-2-enal	-	145	-	-	-	1.4	-
1030	C8-(E)-2-enal	-	-	100	50	-	-	+
1098	C9-(Z)-2-enal	-	300	225	100	4.1	-	+
1130	C9-(E)-2-enal	-	3	10	40	-	5.8	2.7
1236	C10-(E)-2-enal	-	25	1	50	-	-	-
Total ($\mu\text{g}/\text{kg}$)		1002	1448	1216	1890	21.3	10.6	5.5
<i>Alkadienals</i>								
936	C7-(Z,Z)-2,4-dienal	-	60	15	5	-	-	-
970	C7-(E,Z)-2,4-dienal	-	5	20	15	26.4	-	-
1000	C7-(E,E)-2,4-dienal	-	-	200	300	36	-	+
1076	C8-(E,Z)-2,4-dienal	-	90	50	40	-	-	-
1041	C9-(Z,Z)-3,6-dienal	-	30	-	25	-	1.2	-
1107	C9-(Z,Z)-2,4-dienal	-	200	100	50	-	-	-
1153	C9-(E,Z)-2,4-dienal	1	5	10	35	-	-	-
1172	C9-(E,E)-2,4-dienal	-	-	50	30	-	4.7	-
1125	C9-(E,Z)-2,6-dienal	-	5	10	75	3.2	17.2	8.0
1257	C10-(E,Z)-2,4-dienal	-	250	10	100	-	+	-
Total ($\mu\text{g}/\text{kg}$)		1	425	467	675	65.6	23.1	8.0

(Table 1 continued)

RI	Compound	Sardine				Fishes*		
		raw	salted	boiled	canned	raw	raw	boiled
		A	B	C	D	(3)	(1)	(5)
<i>Ketones</i>								
660	C5-2,3-dione	-	-	1	300	49.8	-	140
709	C5-1-en-3-one	2000	45	450	2100	12.2	-	-
760	C6-2-one	-	80	50	100	-	-	-
860	C7-2-one	5	15	450	150	-	3.2	-
958	C8-2-one	-	5	-	-	-	1.0	-
947	C8-1-en-3-one	2	15	5	5	20.1	2.6	0.6
962	C8-1,5-dien-3-one	2	100	450	20	-	1.3	0.36
1015	C8-3-en-8-one	-	-	20	50	-	-	-
1035	C8-3,5-dien-2-one (isomer 1)	-	2	75	50	4.8	-	-
1064	C9-2-one	-	5	-	-	-	-	-
1072	C8-3,5-dien-2-one (isomer 2)	2	300	200	200	3.4	-	-
Total ($\mu\text{g}/\text{kg}$)		2011	567	1701	2975	90.3	8.1	140.7
<i>Alcohols</i>								
750	C5-1-en-3-ol	200	200	250	250	49	9.5	-
876	C7-1-ol	3	150	400	50	-	-	-
965	C8-1-en-3-ol	4	3	20	20	110	18.6	-
1083	C9-3-en-1-ol	-	300	225	190	-	-	-
1161	C9-1-ol	-	-	50	35	-	0.8	-
Total ($\mu\text{g}/\text{kg}$)		207	653	945	545	159	28.9	-
<i>Miscellaneous</i>								
710	Pyrazine	-	-	-	20	-	-	-
728	Dimethyldisulfide	-	-	-	30	-	-	-
890	Methional	-	-	+	5	-	-	5.8
927	Benzaldehyde	-	-	-	150	3.3	1.0	-
1004	Phenylacetaldehyde	-	-	5	10	-	-	-
1200	n-Undecane	30	42	45	50	-	-	-
1400	n-Tetradecane	100	100	110	120	-	-	-
1500	n-Pentadecane	2100	1800	2100	2000	-	-	-

* (3) - raw emerald shiner, (1) - raw whitefish, (5) - boiled trout

We compared the different classes of organic compounds in volatiles. In Table 1 retention indices (RI) and concentration of saturated alkanals found in samples A, B, C and D are given. The results were compared with raw saltwater fish emerald shiner [3] and freshwater whitefish [1] and boiled trout [5]. The total content of alkanals is 14 times higher in saltwater sardines than in emerald shiner. As one can see from Table 1 the level of concentration of volatiles in sardines was on 1 - 2 order more than in other saltwater and freshwater fishes. In processed sardines number and concentration of alkanals were higher than in raw sample. The highest concentration of alkanals was in canned sardines (2 - 2.5 times more than in raw and salted samples).

In raw sardines there are only two alkenals: a large quantity of 3-methyl-2-butenal and traces of (Z)-2-hexenal. Volatiles of processed sardines are rich in alkenals C6 - C9. In emerald shiner, whitefish and trout there are only 3-4 representatives of alkenals (see Table 1). It is interesting to note that in samples of processed sardines we found (E)-2-hexenal, (E)-2-octenal, (Z)-2-octenal and (E)-2-nonenal which have not been found earlier in volatiles of saltwater fish [1-3]. As a whole unsaturated alkenals are found in 48 times more in sardine volatiles than in emerald shiner. 3-Methyl-2-butenal, (Z)-2-hexenal, (E)-2-hexenal, (E)-2-heptenal and (Z)-2-nonenal may be an indicator of processed sardines.

In raw sardines only one nonadienal in concentration of 1 ppb was found. But in processed sardines 10 alkadienals were identified (Table 1). We suppose that it is the main characteristic of sardine volatiles in comparison with other fishes, where 3 or 4 representatives of dienals were found earlier [1- 6].

Total content of alkadienals was comparable with salted and boiled sardines. But in canned sardines the alkadienal concentration was 1.5 times higher. As it is known (E,Z)-2,6-nonadienal and (E,Z)-2,4-decadienal have very low threshold values. Their content in canned fish was 75 - 100 $\mu\text{g}/\text{kg}$. Calculated odour activity values are 750 and 200, respectively. These values were significantly higher than for other substances. We suppose that alkadienals play the most important role in aroma formation of processed sardines. In contrast to others saltwater fish the presence of a large quantity of (Z,Z)-2,4-nonadienal and (E,Z) - 2,4-decadienal is specific and distinctive for salted, boiled and canned sardines.

Qualitative and quantitative composition of ketones (as it is seen from Table 1 is more rich for all processed sardine samples in comparison with other species of fish investigated by Josephson et al. [1-3]. In raw sardines there are only five ketones and pent-1-en-3-one is present in an unusual large quantity. In processed samples ten alkanones are present. Unsaturated ketones C8 are the most interesting for odour formation of sardines. Oct-1-en-3-one has mushroom-like odour, octa-1,5-diene-3-one has geranium-like odour. They have been found in salt- and freshwater fishes [1-3]. Prostaglandins may be their precursors. These ketones are responsible for the fresh, heavy, plant- like note in the aroma of raw fish. The content of C8 - unsaturated ketones in raw sardines, emerald shiner and white-fish is the same but in processed sardines their concentrations were 20 - 400 times higher than in raw white-fish and boiled trout (Table 1). A large concentration of pent-1-en-3-one, octa-1,5-diene-3-one and octa-3,5-diene-2-one may be used as indicators of sardines.

The group of alcohols C5 - C9 was found in sardine volatiles. Two saturated and three unsaturated alcohols were identified in different sardine samples (Table 1). Pent-1-en-3-ol has been identified in all samples in large concentration. Non-3-en-1-ol was found only in processed sardines in large quantity. It was not found in any other fish. Oct-1-en-3-ol has mushroom-like odour and was found in all samples but its content in boiled and canned sardines was more than in raw and salted samples (5-7 times). Unsaturated alcohols take part in flavour formation of processed sardines. Concentrations of alcohols C5, C7 - C9 found in raw and processed sardine are much higher than in other fishes, as it is seen from Table 1. Pent-1-en-3-ol, heptan-1-ol and non-3-en-1-ol may be indicators of processed sardines.

A group of substances was not identified, but characterized by MS data and the values of retention indices. In salted, boiled and canned sardines two substances with retention indices 813 and 819 have not been identified. MS data (M/x : 39, 67, 81, 68, 53, 55, 110, 95) show that they are probably octadienes obtained from octenols. In all samples of processed sardines we found 4 substances with retention indices 803, 898, 904 and 921 i.u. on SE-30. They have the same mass spectra: M/z 73, 61 and 45, molecular ions were absent. The concentration of substance with retention index 803 was maximum in all samples (18 - 41 mg/kg). These substances were not identified.

In canned sardines additionally pyrazine, dimethyldisulfide, methional, benzaldehyde and phenylacetaldehyde were identified (Table 1). In all samples of sardines the n-alkanes C12, C14 and C15 were identified, too (Table 1).

Conclusions

For the first time qualitative and quantitative composition of aroma compounds of raw, salted, boiled and canned sardines has been studied. As a saltwater fish the sardine is very rich in volatiles. Quantification showed the concentration of aroma compounds in processed sardines is one - two orders more than in other species of saltwater and freshwater fishes. The number of carbonyl containing substances (saturated and unsaturated) indicated only 13 substances in the raw sample, but increased up to 36 in boiled and canned samples. Obtained results have been very useful for studying the storage of salted and canned sardines and allowed to find indicator compounds connected with the quality of the stored product. Hexanal, heptanal, nonanal, (E)-2-hexenal, (E)-2-heptenal and (Z,Z)-2,4-heptadienal may be chosen as indicator compounds of processed sardines.

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CHEMICAL SPECIATION OF HEAVY METALS IN SOILS BY SEQUENTIAL EXTRACTION METHOD

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Introduction

There are two principle sources of heavy metals in soils: the anthropogenic input and liberation from the basic rock. Our knowledge of the amounts of these elements, however, does not provide information on the ecological risk involved, as it does not determine their potential for release and biological influence. Anyway, the most important property of this point of view is their mobility and bioavailability, which depends on the chemical compounds are present and the mineralogical composition of the soil. Identification of the chemical compounds of the metals in the soils is difficult and is usually carried out by the chemical speciation analysis.

The term "speciation" has been defined as the determination of a specific form (monoatomic or molecular) or configuration in which an element can occur or to a distinct group of atoms consistently present in different matrices [1]. The point of speciation analysis is in the selective dissolution of the components of soil or exchanging or desorbing the metal ions that are bound to them. Obviously the expected result depends on the character of used solutions and selected procedure. Several single and sequential extraction schemes have been described and increasingly used over the last ten years [1- 4]. The advantage of single extraction is that every solution meets the fresh soil sample. In sequential extraction the step-wise stripping of metal ions takes place from the sample what is already influenced during extraction with the previous solutions and is more or less changed if to compare with the initial sample. Both of two methods will give useful information and complement each other.

The typical extraction schemes promise to identify exchangeable and loosely bound elements, adsorbed elements, easily and hardly reducible elements, easily and hardly oxidizable elements and not extractable part of the element. Usually the main structural units of soil are humus, clay and sandy minerals, carbonates. Humus as well as clay may be considered to have a colloidal organization, where the highly charged anion (micelle) is surrounded by adsorbed cations, mainly calcium and magnesium but also the trace mainly divalent cations.

Usually these elements can be most easily released for instance with alkaline EDTA solution or alkaline acetate buffer. Calcium and/or magnesium carbonates usually contain in their crystalline structure several divalent metallic ions (lead, zinc, manganese etc.). Carbonates are soluble in the weakly acid solutions as acetate buffer with pH 4 - 5. Iron and manganese compounds can be dissolved mainly in the reducible conditions. In both cases the solubility of the compounds with lower oxidation state is higher. Iron as well as manganese belongs to the lithogenic part of the soil, but, usually exists also as amorphous oxide or hydroxide with high specific area and is capable to bind several trace elements. Fe(III) and Mn(IV) substances are reduced to more soluble Fe(II) and Mn(II) substances by such reductants as hydroxylamine or oxalate. In the oxidizing conditions the dissolution of the elements fixed as sulphides or incorporated in the stable forms of humus, takes place. The usual oxidants are nitric acid and hydrogen peroxide. Untouched by extraction remain the elements belonging to the lithogenic silicate part of soil.

Experimental part

In this paper the speciation analysis has been used for the soil samples what contain different amount of the strongly alkaline oil-shale ash. Total concentration of heavy metals was analysed by AAS after melting the sample with sodium carbonate, eliminating the silicon with hydrofluoric acid and dissolving the sample in hydrochloric acid.

Extraction was carried out with the finely ground and at 40 °C dried sample. Weight of the soil sample was 1 g. Volume of the solution was 20 ml. The solution was added to the soil sample and left overnight. Next morning pH of the suspension was checked and regulated if needed. The suspension was shaken 6 hours in a closed polyethylene vessel. In the next morning the solution was separated and the

concentration of heavy metals was determined by AAS spectrometry by the conventional flame analysis. In the sequential analysis the insoluble sample left after the extraction was used again in the next extraction step. In the single extraction a fresh soil sample was used for each step.

Table 1. Solutions used for extraction of Pb, Cu, Zn, Mn, Fe, Cr and Mg from the strongly alkaline soil.

Nr. of step	Composition of the solution	Structural part of soil hypothetically forced by the solution to release the metallic elements
I	EDTA 0.05M, pH 10 (NH ₃ , H ₂ O/HCl)	External surface of the micelles of humic colloids
II	Ammonium acetate 1 M (CH ₃ COOH), pH 4.8	Carbonates, oxides, hydroxides, adsorbed phases
III	Hydroxylamine-chloride 1 M, pH 2.4 (HCl)	Easily reducible phases
IV	Ammonium oxalate 0.2 M, pH 3.0 (H ₂ C ₂ O ₄)	Reducible phases
V	Hydrogen peroxide 15 %, pH 1.3 (HNO ₃)	Oxidizable phases

Table 2. The characterisation and chemical composition of soil, oil-shale ash and the mixtures used in the experiment.

Object of study	Pb mg/kg	Cu mg/kg	Zn mg/kg	Mn mg/kg	Cr mg/kg
Forest soil*	22	21	41	320	72
Fly-ash of oil-shale	132	70	101	484	71
3 part of soil+1 part of ash	50	33	56	361	72
1 part of soil+1 part of ash	77	45	71	402	71

* Forest soil from West Virumaa, 0 - 4 cm horizon, $pH_{KCl} = 4.9$, $c_{org} = 4.9\%$

All four objects in the Table 2 were analysed by sequential and single methods of the extraction with five solution (Table 1).

By using the single method of extraction the scheme of the calculation of partitioning of metals between the soil components is more complicated and different for different metals. Class A (Table 3) represents elements that are adsorbed or exchanged and dissolved in weak acid (acetate buffer) in step I + II for sequential analysis or step II for single analysis.

Table 3. Partitioning of metals in the soil components by sequential analysis (percentage of total concentration).

A (Step I + II)	CARBONATES AND/OR LABILE ORGANIC
Soil	59% Pb, 16% Cu, 9% Zn, 71% Mn, 18% Cr
Ash	26% Pb, 10% Cu, 25% Zn, 45% Mn, 54% Cr
3 p. of soil + 1 p. of ash	27% Pb, 15% Cu, 16% Zn, 41% Mn, 29% Cr
1 p. of soil + 1 p. of ash	20% Pb, 14% Cu, 20% Zn, 46% Mn, 42% Cr
B (Step III + IV)	REDUCIBLE Mn AND Fe OXIDES/ HYDROXIDES
Soil	-% Pb, 29% Cu, 1% Zn, 13% Mn, 10% Cr
Ash	11% Pb, 3% Cu, 11% Zn, 21% Mn, 29% Cr
3 p. of soil + 1 p. of ash	25% Pb, 12% Cu, 13% Zn, 27% Mn, 24% Cr
1 p. of soil + 1 p. of ash	36% Pb, 9% Cu, 18% Zn, 29% Mn, 25% Cr
C (Step V)	HUMIC RESISTANT COMPOUNDS AND SULPHIDES
Soil	3% Pb, 3% Cu, 5% Zn, 3% Mn, -% Cr
Ash	6% Pb, 2% Cu, 6% Zn, 2% Mn, 17% Cr
3 p. of soil + 1 p. of ash	9% Pb, -% Cu, 8% Zn, 4% Mn, 11% Cr
1 p. of soil + 1 p. of ash	6% Pb, -% Cu, 4% Zn, 2% Mn, 9% Cr
D (Total - I-II-III-IV-V)	IN SILICATE LATTICE
Soil	38% Pb, 52% Cu, 85% Zn, 13% Mn, 72% Cr
Ash	57% Pb, 85% Cu, 58% Zn, 32% Mn, -% Cr
3 p. of soil + 1 p. of ash	39% Pb, 73% Cu, 63% Zn, 28% Mn, 36% Cr
1 p. of soil + 1 p. of ash	38% Pb, 77% Cu, 58% Zn, 23% Mn, 24% Cr

As it can be seen in the Figures 1 - 3 there are no essential difference between these two methods of extraction. The second class B is received as the differences III - II or/and IV - II depending on the element. For lead the class B can be calculated by scheme III - II + IV. For copper, zinc and chromium the class B can be calculated by subtracting step II from step IV. For manganese the calculation of the class B can be done by scheme: (III - II) - (IV - II). It is obvious that by sequential extraction in step I and step II the oxidation state of the matter is already changed and the gain of elements with the reducing solution of hydroxylamine and oxalate will differ from that of single extraction. The third class C is calculated as the difference between step V - II, likely for all elements.

Figure 1. The comparison of sequential and single analysis by evaluation of the partitioning of lead.

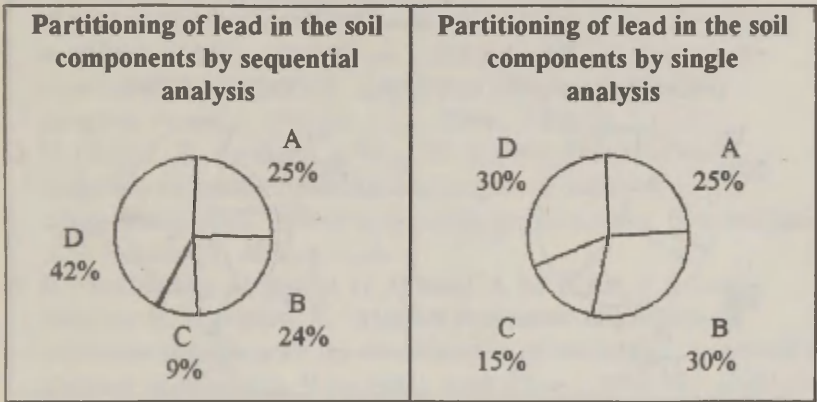


Figure 2. The comparison of sequential and single analysis by evaluation of the partitioning of copper.

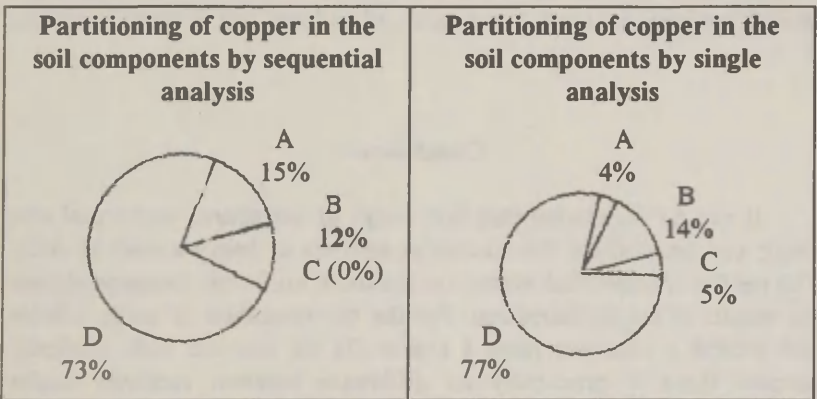
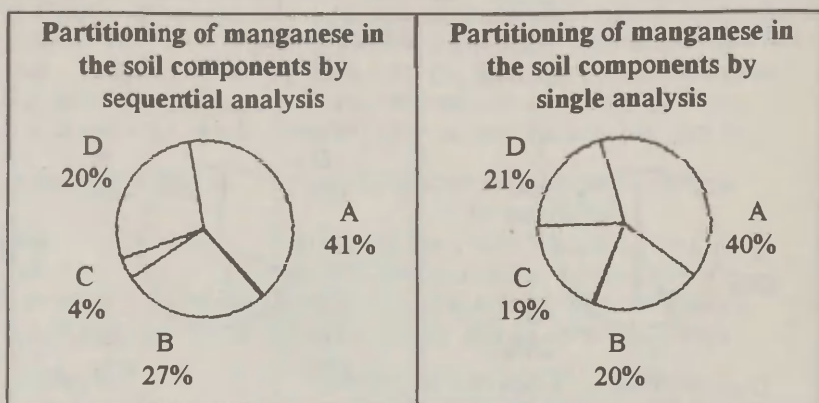


Figure 3. The comparison of sequential and single analysis by evaluation of the partitioning of manganese.



We found that more of each elements is extracted by single than by sequential method. Class D includes this part of metals what is closed in the silicate lattice and what is found as the difference between the total concentration of elements and the sum of A + B + C. The comparison of both methods for the 3:1 mixtures of soil and ash is given in Figure 1 - 3.

Conclusions

It can be concluded that both ways of extraction, sequential and single can be used for the speciation analysis of heavy metals in soils. The results of sequential extraction are more uniformly interpreted than the results of single extraction. For the determination of easily soluble and available elements (step I and/or II) we can use both methods, because there is practically no difference between received results (Figures 1 - 3). In the same time the total gain of soluble heavy metals is greater by using single extraction.

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OIL SHALE ASHES AS COAGULATING AGENT FOR SLUDGES AT THE BIOTREATMENT PLANT

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The coagulation of sludges in secondary settling basins after aeration tanks in the water treatment process still remains the ineffective step of the biotreatment process and causes high levels of BOD and nutrients in the treated water. It is possible to use chemicals for that purpose and make the coagulation of sludges more effective, but it is a rather expensive way of doing it and even small amounts of chemicals will be used, impacts to the environment still appear.

In this work an attempt has been made to use oil shale ashes as coagulant for treatment plant sludges, adding ashes in different amounts to the sludge to find out the most suitable sludge/ashes ratio to reach optimum results in the settling process measuring sludge index, BOD_7 , phosphorus removal and change in pH of treated water with respect to the need for slaving the pH value. There were used two different types of oil shale ashes (cyclon and electrofilter) to compare their influence to the settling process parameters. Ashes of oil shale, which form a very harmful storage district at the North-East of Estonia, are remainder products of electric power station. As the ashes had different properties (particle shape and size), it was assumed, their behaviour in the coagulation process will be different, too. The experimental data showed no any essential differences between two types of ashes, but it will be much more easier to handle with the ashes with bigger particle size. The amount of phosphorus removed depended on the amount of ashes used at the coagulation. Analyses were carried out by adding 0.5 - 5.0 g of ashes per liter of sludges and the decrease in phosphorus content was found to be approx. 70 % from the initial value. At the same time, by adding 3 g ashes per liter of sludge, the pH of sludge was changed from 7.4 till 8.6. The sludge index was measured in time within 150 min (standard values for index are calculated from the settling data at 30

min after coagulant addition and stirring) and the values found were within 50 - 110 ml/l (at 3 g/l ashes added).

It was tried to use bigger amount of ashes for the sludge settling process (5.0 g/l and more), but it was difficult to precipitate the sludge due to a sludge plug at the top of the settling vessel which didn't disappear even at stirring the mixture carefully after adding the ashes to the sludge.

It was tried to use in the role of coagulant the clarified solution, prepared the same way, by adding ashes to the sludge. The residual phosphorus in the treated water was found to be 2.8 mg PO₄ -P/l (initial value 8.5 mg/l), when the ratio of clarified solution and sludge was 1:1.

The coagulation rate of sludges depends also from the suspended solid content in the sludge. The settling of the sludges with suspended solids content more than 5.0 mg/l had very low speed and high sludge indexes.

Removal of BOD₇ was measured for different sludges (content of suspended solids from 3.0 g/l till 5.2 g/l) and at different amounts of ashes added (0.4 - 1.0 g/l). BOD₇ removal made up 85 % for 1 hour settling process and 88% for 3 hour settling with 0.4 g/l ashes added and 77 % for 1 hour and 94 % for 3 hour with 1g/l ashes added. Results of phosphorus removal at same conditions were only in the range 8 - 33 %. The pH change in this case was only 0.08 pH units.

From this point of view it is more reasonable to use low concentrations of oil shale ashes to avoid the increase in pH values of the treated water through the phosphorus content stays too high to discharge the water to a natural recipient. Phosphorus removal could get high values after tertiary treatment stage in bioponds, where there is measured the residual phosphorus contents at the level below the allowed concentrations [1].

In this work it is found that using the remainder product of electric power station, oil shale ashes, as a coagulating agent it is possible to improve the settling properties of sludges at water treatment plant.

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EDUCATIONAL PROGRAMMES ON ENVIRONMENTAL ANALYSIS INTO ACADEMIC GYMNASIUM AND CHEMICAL DEPARTMENT OF St.-PETERSBURG STATE UNIVERSITY

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Academic Gymnasium is structural link of St.-Petersburg State University. The principal contingent of scholars involves fifteen-seventeen years old childrens disposed to natural sciences. The programme of the form of chemical specialization among an elevated theoretical background and special laboratory's practise contains the big division of topics dedicated to ecological problem of chemistry. A strategy and a tactics of environmental analysis are discussed with a fixed attention.

Such elaborated and realised programme for scholars on environmental analysis involves several co-associated blocks, namely lectures (24 hours) - creative seminare (12 hours) - laboratory modules (60 hours) - execution of independent research.

Lectures and laboratory study are carried out by professors and instructors of university. The programme of lecture's cycle contain topics of the form: *The chemistry of an atmosphere, Climatic modifications and acid rains, Prioritical pollutants and possible ways of its generation, Ecological monitoring of environmental subjects, Sampling and chromatographical methods of analysis.*

Creative seminars - solution of different practical problems, *ecological games.*

Practical work first and foremost are pointed to familization with chromatographic methods (TLC, GC, HPLC), also spectral method and using ion-selective electrodes.

Subjects of scholar's research work: *Mains ecotoxicants of drinking water and detection methods, Determination of pesticide in melted*

snow and in a sewage, Determination of carbonyl compounds in atmospheric air.

Scholars came to an end of Gymnasium courses as a rule continue on in the university started before study up to and including diploma and dissertation works.

In its turn in the university's programmes for students choose the specialization *Organic analysis* physico-chemical methods of environmental analysis has received much attention.

Lecture and agreed laboratory courses of gas and liquid chromatography, functional organic analysis, spectral methods, physico-chemical methods of substance separation, using of computers in organic analysis also oriented to ecological problem of chemistry diploma works makes possible to give to students an adequate background for further independent work in the field of environmental analysis.

DETERMINATION OF FORMALDEHYDE IN AIR INSIDE OF BOOK STORAGE ROOMS OF LIBRARY OF RUSSIAN ACADEMY OF SCIENCES (St.-PETERSBURG) BY GAS AND LIQUID CHROMATOGRAPHY

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The most common method of determination of formaldehyde's trace quantities in environment is one's chemisorbatic concentration in the form of 2,4-dinitrophenylhydrazone (2,4-DNPH) with following HPLC analysis [1].

A reagent for derivatization - 2,4-dinitrophenylhydrazine - is coated as an example on Silicagel C-16 placed in the polyethylene cartridge (it is possible to use the cartridge production by the firm "Diapak") from the acetonitrile solution with a supplement of phosphoric acid. 2,4-dinitrophenylhydrazone of formaldehyde obtained in a result of one's chemisorption is eluates from the Silicagel C-16 surface by acetonitrile with following HPLC analysis. Named method of analysis was used to measuring of formaldehyde's contents in air inside of book storage rooms of Library of Russian Academy of Schiences (St.-Petersburg) as a check one.

A new alternative version of formaldehyde's determination in air through the selective and quantitative transformation of it in hexamethylentetramine now is suggested by us that open the possibility of a simple and sure registration of formaldehyde by the use of gas chromatographic analysis with universal flame-ionization detector of (it is better) selective nitrogen-phosphorus detector.

It has been known that formaldehyde molecules react readily with ammonia in polar mediums giving hexamethylentetramine as a single product with a quantitative yield [2].

There are two possible techniques to put in practice this reaction for selective derivatization of formaldehyde: air sampling is performed directly by passing 10 - 20 l of air at a rate 0.5 - 1.0 l/m through water solution of ammonia or through cartridge with a Silicagel impregnated by Polyethylene glycol 400. In the last case formation of hexamethylentetramine takes place during elution of formaldehyde by water solution of ammonia.

In the paper of Japanese authors [3] the interaction between gaseous formaldehyde and ammonia was applied for subtracting of formaldehyde from complicated vapour-gas mixture. However quantitative evaluation of conversion has not been discussed. For checking yields of hexamethylentetramine in our conditions the artificial vapour-gas mixtures of formaldehyde in air was prepared and analysed by using of discussed type of derivatizations and liquid and gas chromatographic registration of derivatives (Table 1). Presented data illustrates that a conversion of formaldehyde into hexamethylentetramine is close to quantitative in the range under study.

Table 1. Determination of formaldehyde in artificial vapour-gas mixtures

Given mg/l	MIC	Found, mg/l (n = 3; P = 0.95)	Analytical method *
0.029	0.8	0.023 ± 0.003	A
0.112	3.2	0.093 ± 0.003	A
0.154	4.3	0.134 ± 0.004	A
0.290	8.2	0.283 ± 0.003	A
0.380	10.8	0.320 ± 0.003	A
0.032	0.9	0.027 ± 0.004	B
0.131	3.7	0.118 ± 0.003	B
0.159	4.4	0.142 ± 0.003	B
0.310	8.8	0.291 ± 0.004	B
0.420	11.9	0.402 ± 0.004	B

* A - HPLC; B - GC.

The control set of data concerned with analysis of air inside of book storage rooms has been performed in two mode of operations

incorporating traditional and new methods. Table 2 lists obtained results. It is possible to see that values of determination of formaldehyde deduced from suggested method and standard HPLC analyse of 2,4-DNPH are in a good agreement.

Table 2. Determination of formaldehyde in air inside of book storage rooms of Library of Russian Academy of Sciences

Sampling place	The technique of sampling	The type of derivate, the method of analysis	Found, mg/m ³
Room No 11	Absorption in the film of PEG 400	HMTA	1.15
		GC	0.96
	Chemisorption by 2,4-DNPH*	HMTA	0.85
		LC	1.05
Room No 11b	Absorption in the film of PEG 400	HMTA	0.70
		GL	0.88
	Absorption in the water sol. of NH ₃	HMTA	0.58
		GL	0.45
	Chemisorption by 2,4-DNPH*	HMTA	0.92
		LC	0.84

* by 2,4-DNPH is denoted 2,4-dinitrophenylhydrazine

A precision and an accuracy of results obtained through the using of the new mehtod is not worse of 15 - 20 %.

Obtained data testifies that now (sevenyears after big fire in 1988) air inside of book storage rooms of Library of Russian Academy of Sciences is highly polluted by formaldehyde. This situation requires accepting of eexecuted program on keeping or health of library's staff.

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STRIPPING ANALYSE OF HEAVY METALS IN WATERS OF ESTONIA

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As a result of high sensitivity, stripping analysis is one of the techniques, that is sufficiently sensitive to determine trace elements directly in natural waters without previous concentration. Because of the complicated composition of natural waters (metals, ligands, surfactants ect.) and low level of the metals in samples, stripping analysis presents several problems to the analyst. Usually there are noted two types of interferences, the adsorption of organic matter onto the electrode and formation of intermetallic compounds. A large number of organic compounds are able to adsorb and in addition of their effect on the stripping peaks because of their influence on the kinetics of the electrochemical processes, they cause adsorption-desorption peaks, especially if the pulse stripping mode is used. For destruction of organic matter, UV-irradiation of the sample, acidified previously to prevent adsorption of the metal ions on the walls of the sample container, is usually used.

Intermetallic interferences cause the decreasing of the stripping peak of a more electronegative metal, for example, zinc in the presence of copper or nickel. The best way to overcome this problem is by adding the "third metal" to the sample, for example, gallium. In addition to this care must be taken to avoid the saturation of mercury because of low solubility of metal in mercury. Well-known are difficulties in case of determination of high copper concentration on the thin film electrode.

In this paper methodics and results of analysis of sea-, fresh- and precipitation waters are presented. Seawater samples were collected during expedition of research vessel Livonia in September 1994, stored in acid cleaned polyethylene bottles, acidified with Suprapur HNO_3 and retained at 4 °C. Before analysis 2 ml of Suprapur 30 % H_2O_2 per liter was added and samples were irradiated with 800 W UV-lamp for 4 hours. Freshwater samples of phreatic waters and lake waters

from Kurtna area (Nord-East region of Estonia). Samples were collected in spring 1995, acidified and the pretreatment was the same as in the case of seawater. Precipitation samples were collected by Geological Survey of Estonia during January- March 1995, filtered, acidified and analysed without UV- irradiation.

Voltammetric measurements were provided with a Tacussel Polaropulse PRG5 analyser in the differential pulse mode with pulse amplitude of 50 mV. The thin film glassy carbon rotating disc electrode (RDE) was employed for the determination of Cu, Pb, Cd and Zn, previously plated thick film electrode for Ni and Co and gold RDE for the analysis of mercury. The sample in a 50 ml quartz cell was purged with argon, pH in the cell was controlled using a solid contact glass electrode coupled to a UT-8806 pH- meter. All reagents were Suprapur grade and previously checked on the content of heavy metals.

Methodics of analyse

Mercury. After polishing a gold electrode was stored in 6 M HNO₃, washed and polarized in oxygen- free 0.01 M HClO₄ at 0.0 V. To the acidified sample (except the seawater one) 50 ul of 1 M HCl was added and the electrode was activated by cycling the potential between 1.0 and -0.3 V. Deposition was provided at 0.15 V during 10 min. The stripping peak occurs near to 0.6 V (S.C.E.) . In seawater the activation was provided between 0.75 and -0.3 V and the peak potential was near 0.5 V. Using these activation conditions the background current occurs like a wide peak with maximum between 0.4 and 0.5 V and while the sensitivity was about 0.01 uA/ng min, the detection limit with 10 min deposition time (τ) is only 2 ng/l with an error of ~ 50 %. Depending on potentials used for an activation of the electrode better backgrounds were obtained, but the sensitivity was sufficiently lower. In case of high iron concentration a wide redox-peak appears near the potential of 0.5V and for masking of Fe sulphosalicylic acid was added into the cell.

Copper, lead and cadmium. To the sample in the cell 100 ul of acetic acid was added and pH value was adjusted to 4.7 with NaOH. The thin film electrode was prepared "in situ" by adding $2 \cdot 10^{-5}$ M Hg(NO₃)₂ to the sample in the cell and depositing at -0.8 V during 5 min. The first scan to 0.1 V was not registered and after that Cu, Pb and Cd were deposited on E= -1.05 V during 2- 10 min depending on concentration of metals. It must be noted that in all cases τ = 10 or 5 min for determination of cadmium had to be used. In more contaminated

samples there was necessary to measure Cu and Pb separately using shorter deposition time to avoid saturation of mercury film with copper and reach better reproducibility of both, Cu and Pb peaks. In some phreatic water samples with very high iron concentration (10 - 100 mg/l and more) there were difficulties to determine of Pb and Cd because of wide peak in the region of these potentials (-0.7 ÷ -0.3 V). For reduction of Fe(III) some crystals of ascorbic acid were added to the sample and analyse was provided at lower pH value (pH = 2.2 - 2.4) to exclude oxidation of ascorbic acid by traces of oxygen in the solution. Detection limits for copper, lead and cadmium were 25, 10 and 10 ng/l with $\tau = 10$ min.

Zinc. For the determination of zinc, the deposition potential of -1.5 V was used and analysis was provided at pH = 4.7 to minimize the background current. Usually it was possible to provide analysis after measuring of Cu, Pb and Cd from the same volume of the sample after adding 10^{-6} mol/l of Ga^{3+} with deposition time of 0.5 - 2 min. In case of very high copper or zinc content (> 10 ug/l) it was necessary to dilute the sample 1:5. In iron-rich waters there were difficulties because of electroreduction of iron on the electrode and decreasing of the hydrogen overvoltage. Masking of Fe(III) with sulphosalicylic acid occurs not effective but the dilution of the sample allows the analysis with satisfactory results.

Stripping peak of Zn occurs near -1.08 V and the scan was stopped at -1.0 V, before oxidation of Ga, otherwise the peak height decreases essentially after every next scan. Detection limit for zinc was about 25 ng/l.

Nickel and cobalt. Previously formed thick film electrode was used for determination of these metals. Deposition of mercury was provided from acidified 10^{-3} or 10^{-4} M $\text{Hg}(\text{NO}_3)_2$ during 2 - 5 min using different regimes of plating potentials. pH of the acidified sample was adjusted to 9.2 with NH_4OH , 10^{-4} M dimethylglyoxime was added and metal complexes were adsorbed onto the electrode at -0.7 V. 45 s occurs to be sufficient for establishing adsorption equilibrium and prolonging of the deposition time did not increase the peak height. Cathodic peaks of Ni and Co were registered at - 1.05 and - 1.17 V. Depending on conditions of formation of the mercury film it was possible to obtain electrodes with higher sensitivity with regard to Ni or Co, but the detection limit was 50 ng/l for both metals.

Some results of the analyses of waters are presented in Tables 1- 4. All contents in ng/l.

Table 1. Phreatic waters from the Kurtna area.

Bore Nr.	Cu	Pb	Cd	Zn	Hg	Ni	Co
51	120	190	33	4750	28	680	200
32	290	435	55	3900	12	400	150
00632	1600	460	50	13000	30	1280	500
00699	30	130	10	2800	10	320	100
7312	145	200	20	7800	170	1000	300
218	10600	18600	32	31200	50	760	250
00622	130	620	40		400	3300	500
00640	1660	1800	45	65000	350	3000	1700
215	76800	134000	<100	117000	400	14700	4700
KPP	580	210	35	130000	15	3600	720

Table 2. Lake waters from the Kurtna area.

Sample Nr.	Cu	Pb	Cd	Zn	Hg	Ni	Co
107	780	765	120	5200	20	550	200
111	380	445	26	5000	20	600	200
123	145	345	25	4850	25	700	200
128	700	350	30	3100	30	520	80
135	375	470	35	7150	80	600	150
138	380	135	18	3950	100	1130	200
142	1070	555	55	7310	120	440	80

Table 3. Precipitations.

Sampling point	Cu	Pb	Cd	Zn	Hg
Narva	3150	190	130	58500	5
Sõrve	3490	600	40	350000	10
Kuusiku	3275	580	110	884000	15
Ristna	10050	2070	235	520000	10
Ruhnu	3400	1000	60	16800	3
Haanja	8820	1240	82	13000	8

Table 4. Seawater.

Sampling point	Depth, m	Cu	Pb	Cd	Zn	Hg
LL- 7	1	1200	540	65	5800	40
LL3Q	1	1200	680	22	3540	12
GR- 18*	10	230	135	31	3800	16
K- 1	1	1200	260	55	8500	24
K- 5	1	1195	270	55	8450	24
K-8	1	1195	340	20	5850	16

* - sample GR- 18 was filtered through 450 nm Nucleapor- filter before acidification.

Some samples were analyzed parallelly using atomic absorption spectrometry. Good agreement was observed between both methods except for Zn, where results got with stripping voltammetry occurs to be somewhat higher.

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SOLAR CELLS BASED ON DYE-SENSITIZED NANOSTRUCTURED TiO₂ ELECTRODES

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Introduction

Nowadays the problem of energy production becomes more and more important in all over the world. This is for example due to the decreasing resources of mineral wealth. Moreover, the production of energy have always been connected with environmental problems. For energy production in Estonia the oil-shale industry is to a large extent used, which remnants has caused big pollution of water, sediments and air. But there is one energy source that works reliably, free of charge and at safe distance: the sun. The energy we receive from the sun is tremendous, being about 7000 times higher than we consume. The problem of solar cell energy production today is not its high land requirement, but rather its high cost. Energy produced by a silicon cell is about 10 times more expensive than conventional energy. A big interest for preparation of so called photoelectrochemical (PEC) solar cells - converting solar energy to electrical or chemical energy - emanated in the early 70's from the work by K. Honda and A. Fujishima from the University of Tokyo [1]. In a PEC cell a semiconductor is in contact withan electrolyte forming a solid/liquid interface and in the Honda-cell water was oxidized to oxygen by illumination of a titanium dioxide semiconductor electrode. Since a solid/liquid contact is easy to establish it was believed that cheap, e.g. polycrystalline, materials could be used for PEC devices and during the years several different types of cells were worked out. Since solar cells (or photovoltaic cells, PV) has not been studied in Estonia yet, the research in this field will be interesting and important to follow. Especially, if there is a possibility to find PV cells producing energy with low cost and what is most

important - with clean environment. However, up to now the main problem of most PEC cells has been their lack of long stability. It has been found that semiconductors with suitable band gap energies, i.e. the threshold energy to absorb light, corrode in the electrolyte during illumination [2]. One way of getting around this problem would be if it is possible to red-shift the absorption spectrum of stable large band-gap semiconductors into the visible region. This can be done by e.g. dye-sensitization, but a problem found in the earlier studies of this approach was that of poor light harvesting. On a smooth surface, a monolayer of the dyes with even the highest extinction coefficients absorb less than 1% of incident monochromatic light. The use of multilayers of the sensitizer was unsuccessful, the outer layers acted just as a light filter.

The break-through by Grätzel and coworkers (at the Swiss Federal Institute of Technology) in preparing efficient dye-sensitized PEC cells came with the use of high surface area TiO_2 semiconductor electrodes, so called nanostructured semiconductor electrodes. These electrodes are made from a colloidal solution with nanometer sized particles of TiO_2 , forming a nanocrystalline-nanoporous electrode with a very high internal surface area. The roughness factor, defined as the ratio between the real and projected surface of the film is e.g. for a $10\ \mu\text{m}$ thick film about 1000, meaning that the absorbance from a monolayer of the dye adsorbed on the nanostructured TiO_2 film is increased by the same figure. The light harvesting in this so called Grätzel-cell is therefore almost 100% at the absorption maximum of the dye and a 10 % efficient cell in simulated solar light (one sun AM 1.5) has been prepared [3, 4].

In the sensitized colloidal TiO_2 film electrodes $\text{Ru}(\text{bpy})_3$ -complexes are normally used as dyes forming the photoanode in the PEC cell and the counter-electrode is composed of glass covered with a conducting oxide layer and a catalytic amount of platinum deposited on the oxide layer. Light absorption is performed by a monolayer of the dye adsorbed chemically to the semiconductor TiO_2 surface. The excited dye molecule is able to transfer an electron to the conduction band of the semiconductor. The remaining positive charge on the dye is transferred to a redox mediator (electrolyte with suitable standard potential) present in the solution with which the cell is filled, and thence to the counter electrode. The injected electron in the semiconductor percolates through all the interconnected particles to the back contact - goes to the outer circuit performing work - whereafter it ends up at the counter electrode. The circuit is closed with electron transfer from the counter electrode to the

redox mediator (Figure 1). From a fundamental point of view all processes within this circuit are not fully understood and need complementary studies [3-7].

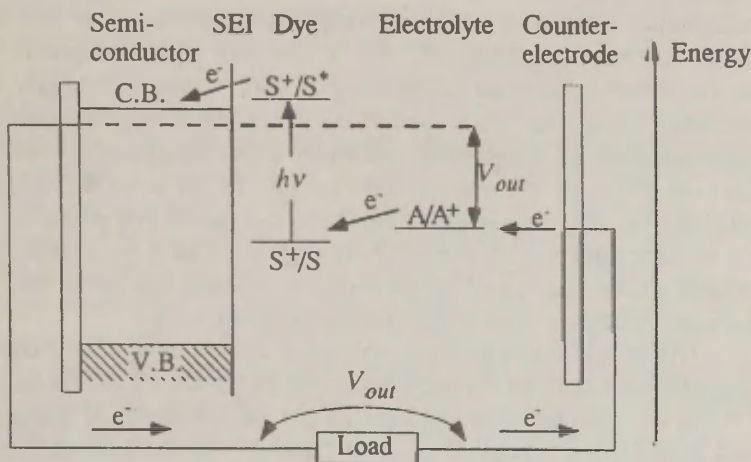


Figure 1. Scheme of the dye-sensitized photoelectrochemical cell.

The aim of this paper is to introduce the working principles of the Grätzel cell. The preparation of the cells is described. The experiments represent preparation of small solar cells modules, varying components and conditions. This is important for developing preparation methods to give high efficiency solar cells and for building up a procedure to check new batches of components routinely. For the characterization of the results photocurrent action spectra was taken. These represent the incident photon to current conversion efficiency (IPCE) as a function of wavelength. Using this calculated quantity final conclusions could be made. To check the reproducibility, experiments were made where two solar cells modules were prepared in parallel.

Preparation procedure

Two different colloidal solutions were used in the experiments; commercial TiO_2 , P25 powder, Degussa AG, Germany and TiO_2 solutions prepared by hydrolysis of titanium-isopropoxid $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ [4]. The 4.8 ml 65 % HNO_3 was added to 600 ml distilled deionized water to obtain $\text{pH} = 1$. Using a dropping funnel the 100 ml 97 %

titanium tetraisopropoxide was added and the reaction mixture was stirred in a waterbath (80 °C) during 8 hours to evaporate the propanol formed during the reaction. To increase the particle size the solution was autoclaved at 200 or 250 °C for 12 hours. Depending on the autoclaving temperature the resulting nanostructured film will have different optical properties. At 200 °C the film is as transparent as a normal window, whereas autoclaving at 250 °C yields a highly light scattering white film. From the formed homogenous solution water was removed using an evaporation procedure under vacuum (30 - 40 °C) until the TiO₂ content was 13 % by weight. To get crack free films an equivalent of 50 % by weight of carboxyl was added. The preparation of a colloidal solution from the P25 is basically made by grinding the powder adding e.g. acetyl acetone to prevent reaggregation of the TiO₂ particles. This procedure is described in detail in ref. [4].

The colloidal solution was applied as a thin layer onto a conducting substrate, such as F-doped SnO₂ coated glass with the dimensions 1.5 x 2 cm. Scotch tape was used as a mask for electrical contacts as well as providing the film thickness. Typically film thicknesses between 4 - 8 μm were prepared. The colloidal solution was spread out by raking with a glass rod. The sample was fired at about 450 °C for 45 minutes to burn out organic additives and also to provide a mechanically stable film and electrical contact between the particles. This process gives a highly reactive surface for dye adsorption [5]. The porous TiO₂ film was coated immediately after firing with the sensitizer by immersion into a dye solution. The sample was left in the dye solution overnight. The photoanode was ready to use after it was dipped for 10 minutes in pyridin to reduce the dark current. The used dye sensitizer was [Ru L₂(NCS)₂].2 H₂O, where L = 2,2' - bipyridyl - 4,4' - dicarboxylic acid [4]. Ruthenium dyes are preferred in view of good solar light absorption and long term stability. Carboxyl groups on the bipyridine ligands serve for attachment on the TiO₂ surface. The prepared dye solution had a concentration 0.5 mM in dry ethanol.

A counter electrode is placed directly on top of the photoanode and the cell is completed by soaking up a redox electrolyte between the two electrodes and filling the pores of the TiO₂ film. The redox electrolyte was iodide/triiodide (I⁻/I₃⁻) as a redox couple in propylen carbonate and ethylen carbonate in relation 50/50 (v:v). This couple has the great advantage of showing a high overvoltage for reduction on TiO₂ (E = 0.1 - 0.3 V_{SCE} depending on the solvent). The iodide salt concentration

must be rather high to ensure rapid reduction of the dye cation and good conductivity of the electrolyte film. The triiodide concentration is a compromise between providing a good electron transfer reaction at the counter electrode, while at the same time giving a low probability for an uptake of TiO_2 conduction band electrons. In the present report LiI and I_2 with the concentrations 0.5 M LiI and 0.05 M I_2 were used.

As mentioned above, the function of the counter electrode is to transfer the electrons arriving from the external circuit back to the redox electrolyte. The two electron redox couple iodide/triiodide requires a catalytically active counter electrode. Here an electrochemically platinized conducting glass was used. The platinization could also be carried out by thermal decomposition of a thin platinum salt layer. For measuring the photocurrent action spectra LPS 255HR Universal Arc-Lamp Power Suply, Xenon Lamp, 3M photodyne (Model 400 broadband sensorhead) and monochromator (Kratos Instrument AB LAMBDA) were used. The spectrum range was 400 - 800 nm and the photocurrent was registered with an interval of 20 nm. Illumination was performed through the photoanode. The IPCE was calculated as: $\text{IPCE} (\%) = 1241 I/P \lambda$, where I = photocurrent ($\mu\text{A}/\text{cm}^2$), P = light power (W/m^2), λ = wavelength (nm).

Results and discussion

The experimental results showed that the IPCE depended on the autoclaving temperature in the preparation of the colloidal solution. In all measurements the higher IPCE was reached with a colloidal solution prepared at the higher temperature (250 °C). The difference of the IPCE at 540 nm was up to 20 %. Since the autoclaving temperature plays a important role in the size of the formed colloidal particles, larger particles are formed at higher temperatures, this effect can be understood in terms of diffusion problems in the electrolyte for a film constituted by smaller particles due to too narrow pores and/or effects caused by light scattering. Also noteworthy is that the efficiency decreases with oldening of the colloidal solutions. To use freshly prepared TiO_2 colloidal solution is recommended in some papers in the literature [cf. 7].

In comparison between the different preparation of counter electrodes the better results was obtained using electrochemically platinized electrode. But it has been observed that the thermally platinizing method gives more long term stability and since we obtained

only a small difference with the electrochemical deposition the thermal procedure is certainly worthy to investigate further. Figure 2 presents typical photocurrent action spectra. The maximum occurs at 540 nm, which coincides with the absorption maximum of the dye in solution. The IPCE of two samples prepared at the same time, using identical conditions and chemicals, were also measured. The IPCE values of the samples were different in a range of 2 - 3 %, which is a reasonable error limit for these type of measurements. Thus, to compare two solar cells, where one component or one condition is varied in a systematic way, the IPCE values must differ at least 5 %.

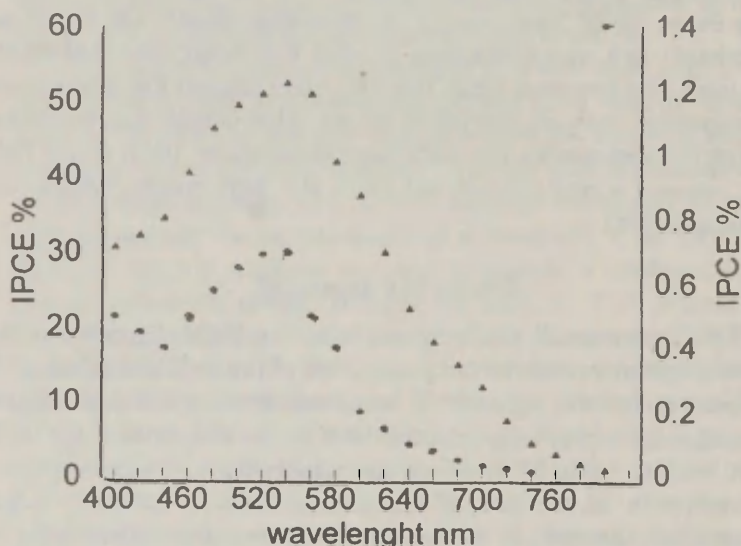


Figure 2. Action spectra of nanocrystalline cells.

▲ TiO_2 colloidal solution, prepared by hydrolysis of titanium tetraisopropoxide, autoclaving temperature 250°C , sensitized with $[\text{RuL}_2(\text{NCS})_2] \cdot 2\text{H}_2\text{O}$, where $\text{L} = 2,2'$ - bipyridyl - 4,4' - dicarboxylic acid.

● sun protection cream, factor 10, as a colloidal solution was used, the same sensitizer. IPCE at 540 nm = 0.75 %.

Final remarks

The so called Grätzel-cell has the opportunity to meet the requirements for the large-scale use of photovoltaics. In four years of research and development an efficiency of 10% in full sunlight has been reached in the laboratory, being already competitive with amorphous silicon cells. The economic perspectives of the Grätzel-cell is also interesting. A study performed by the Research Institute of North Carolina (USA), predicts a cost of 0.60\$/Wp for industrial production of dye-sensitized nanocrystalline cells. This is about a factor of five cheaper than the minimum cost of conventional silicon cells. Such a difference is explained by the lack of technological obstacles (e.g. only an oven is necessary besides chemicals) to production of the Grätzel-cells, together with the low cost of the raw materials required. In order to envisage mass production, a photovoltaic cell must not only be efficient and cheap, it must also be as harmless as possible for our environment and our health. In case of the Grätzel-cell TiO_2 is found in nature and is well characterized, widely used (e.g. as a pigment, in toothpaste and in cosmetic products) and known to be non-toxic. As for ruthenium, used in minuscule amounts in the solar cell, the metal is used as an additive in bone implants and thus is without grave consequences for human health. Another important aspect of a photovoltaic cell is its long-term stability. Degradation of the Grätzel-cell can be due to several factors. However the tests that have been made by Grätzel's group look promising. For example, the dye has been subjected to accelerated stability tests, during which time the dye has performed 50 million cycles, the equivalent of ten years' exposure to the sun. No discernible degradation of the dye was observed.

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FEATURES AND POTENTIALITIES OF ELECTROCHEMICAL TECHNIQUES IN ANALYSIS

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Natural waters are considered the most complex object for analysis. The difficulty lies in the nature of the object, due to the continuous changeability in space and time as of the substances to be denoted, as of the whole system resulting from concurrent physical, chemical and biological processes. Unnatural factors should be regarded here as well. In water a great number of individual substances are subject to determination at 10^{-9} - 10^{-6} M in the presence of different impurities and often without any precise definition of forms of the substances to be determined, as without the correspondence of the forms to the real state of substances in water.

The above and other factors have caused the necessity both of revising some traditional in practice of analysis statements and procedures and elaborating original approaches to water analysis, as well as establishing the most stringent requirements for analytical methods and techniques. Though the above propositions hold true for any method used in water analysis in the present paper we intend to dwell on electrochemical methods only. In analysing waters one should provide a possible solution of the following basic analytical tasks: to assess whether the method and technique employed fit to carrying out proper kinds of determination and prove the validity of the data obtained; to establish the real state of the substance to be determined in water, stating its concentration exactly in the form which the given substance is, if only at the moment of sampling for the substances undergoing changes in water, although these substances prevail; to study

migration and various transformations of substances typical of the water objects at 10^{-9} - 10^{-6} M concentrations; to estimate the complexing ability of waters as well as other generalized indexes of water quality. With respect to the conventional approaches, the technique and the method employed as for the given kind of determinations, as the validity of the data obtained prove to be reliable by the agreement of the results obtained within the given technique and the results coming from the independent methods. In water analyse such a criterion is incompetent because of the results obtained by different methods and techniques, the content of the substance subject for determination may be represented in different forms and, thus, critically differ. Therefore, according to different results one cannot prove the reliability of one or another technique, on the contrary, each technique should state the fixed form of the substance and its correspondence to the state of the substance in the analyzed water. Otherwise, the contradictory results obtained with different methods and techniques do not only exclude the possibility of other techniques having high reproducibility, but quite the reverse, each of the techniques should be regarded as an integral part serving for the purposes of decoding the state of the substance determined in water; these methods seem to be supplementary. Only a number of the supplementary methods and techniques reveal the real state of substances in natural waters, the results agreeing with each other and obtained by adding together the individual forms of the substance and their total content prove validity of the data obtained and the reliability of the method and the technique employed for the given kind of determinations.

Since the results obtained with different methods can demonstrate the concentration of the substance in various forms which can change as in the process of preparing water for analysis, as in the course of the analysis, then to determine the real state of the substance in water, its concentration as well, the analysed water should not be adapted to techniques and methods. The reverse approach is certain to be more correct: adapting methods to the analysed water. It signified that the techniques employed should make it possible to determine directly standard substance forms at the given concentration level without any preliminary treatment of the tested water. We mean that even concentrating and deluting are fraught with a change of the substance state in water and the distortion of the results.

So, according to the routine of testing substances in river waters by means of different methods a calibration chart (CC) is designed in the distilled water rarely on the base of an imitate which is considered close in composition to the water under analysis. Still, it is neglected that employing dilution of the water under analysis may cause some changes in the state of the given component. The experimental use of the techniques should be preceded by designed the CC on the analysed water, the same reagents, standard solutions and procedures stipulated by the method being applied. In case that CC of the distilled and analysed water agree, one may assume that the forms of detecting the given component in these water agree to CC based on the distilled water is suitable for carrying the determinations in the water analysis.

Lower effect on the substance state in water while preparing water for analysis and analysis itself is reached using the different methods, such as differential chronoamperometry (DCA). The main advantage of the DCA in water analysis is the possibility to determine in water different substances at limit concentration without concentrating and any other pretreatment of the analysed water. In DCA the reference solution, not the water, is preliminary treated. The best reference solution, not is the part of the analysed water where the components determined are either transformed into a nonelectroactive form as removed by extraction or by some other means.

Direct methods should be employed for the study of the behaviour of the elements in water in order to distinguish between the free and bound forms of the elements, to evaluate the strength of the compounds formed and the complexing ability of waters. So, it was DCA which helped us to state that the chromium form in river water is determined by the form of its ingress and depends on the redox state of the water; titanium (IV) in lean mineralized river waters does not form stable complexes; nickel (II) and cobalt (II) in lean mineralized waters at the concentration $1.2 \cdot 10^{-7}$ M are found in a free state, while at the concentration $1.2 \cdot 10^{-9}$ - $1.2 \cdot 10^{-7}$ M they are either in a free state or complexed with ligands with lower stability constants than of dimethylglyoximates of nickel and cobalt.

A great number of the above results has been obtained by employing catalytic currents providing rather low concentrations. But every catalytic system has its own threshold concentration limiting the catalyst activity. These threshold effect of the catalyst activity is obvious on the example of chromonitrate system: the linearity of the CC is valid

everywhere within the open range of chromium concentrations when there is no nitrate in the system, while with the nitrate available the same holds for the narrow range of concentrations. The linearity is especially distorted under low chromium concentrations. It has also been shown that the lower chromium concentration, the lower is the effect of the catalyst. Its activity ceasing completely at the definite threshold concentration. Therefore, by determining individual substances in nature waters preference should be rendered to methods providing fixation of a substance in its unchanged form at least in the course of preparing water for the analysis and the analysis itself. However, potentialities of electrochemical methods are not restricted to determining individual substances, especially as they cannot confine themselves determining individual substances only. The results of such a procedure can not give the total evaluation of the water quality. For this purpose one need the total indices, too. One of such value is the self-purifying ability, which in reference to heavy metals is often related to the complexing ability of waters. It is convenient to use electrochemical methods, polarography or voltammetry in particular, for determination the complexing ability of water.

THE BIOLOGICAL PHOSPHORUS REMOVAL AND NITRIFICATION IN WASTEWATER TREATMENT PLANTS

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Introduction

During last years the application of fertilizers in Estonia is decreased and the phosphorus (P) and nitrogen (N) input into rivers and lakes is decreased too. In natural waters not affected by human activity, algal growth is generally limited by insufficient presence of either of these two elements [1]. But the colonial species of cyanobacteria (so-called "blue-green algae") are capable of fixing N from air and then N can not act as growth-limiting element. Nevertheless, it is necessary to reduce the ammonium nitrogen in effluent, above all because the oxygen balance is loaded and the danger of fish toxicity exists. Therefore, high removal of P and nitrification of ammonium N make possible to avoid the eutrophication. Because of the especially toxic effects of blooms of "blue-green algae" in waters with low N supply, it can be preferred to diminish the P concentration in such an extent that P becomes the growth-limiting element [2].

In conventional biological sewage treatment plants the BOD removal is higher than P or N removal. The BOD:N:P removal ratio is 100:5:1 and the method is not sufficient to meet the low effluent P concentrations required to prevent eutrophication. In such treatment process the P and N removal is carried out by incorporation P and N into sludge biomass. In denitrifying plants N is removed as N_2 , but the P removal can only be carried out by incorporation into the solid phase. In sewage plants with EBPR the activated sludges have a high P content. In such plants the activated sludge or mixed liquor must pass alternately through anaerobic and aerobic zones [2, 3].

The dissolved oxygen (DO) concentration is the most important parameter to influence nitrification process. The effect of DO concentration on the rate of nitrification has been investigated by a number of researchers [4 - 9]. The wide range of nitrification rates with varying DO concentrations is reported. Anaerobic zone residence times in EBPR process may be supposed to influence the growth possibilities of nitrifying organisms. However, there are observations that even 24 hours anaerobic retention time does not affect nitrification significantly [2], but in existing EBPR plants this time is not so long.

Temperature is a second important factor influencing the nitrification. The growth constants of nitrifying bacteria are affected greatly by temperature, the optimum temperature appears to be in range 28 -36 °C and for nitrobacter up to 42 °C [10]. Thus, nitrification must proceed better in warmer seasons. Still, nitrifying activity in natural lakes in surface waters was maximal at overturn or during the winter circulation period [11].

The high nitrification rate in EBPR plants without denitrification enlarges recycle sludge nitrate content. Influent domestic sewage is normally devoid of nitrates. Recycled nitrates influence on the creation of anaerobic conditions and the anaerobic zone residence time must be longer.

Experimental

The activated sludges were obtained from the Põlva and Viiratsi sewage treatment plants, operating with high energy density aerators. In these plants some features of EBPR process were revealed [12,13].

The nitrification rate of the activated sludges was determined accordingly ISO 9509 Annex A. The nitrate concentration was measured with nitratemeter HM-002. The nitrification rate in milligrams of N per gram hour was calculated as follows:

$$(c_1 - c_0)/MLSS \cdot 4,$$

where c_1 is the concentration of nitrate, in milligrams per litre, in the reaction mixture after 4 hours;

c_0 is the concentration of nitrate in the mixture plus reference inhibitor (allylthiourea), after 4 hours;

MLSS is the concentration, in grams per litre, of mixed liquor suspended solids in the test flask.

For all determinations the activated sludges were centrifuged and washed with distilled water or with nitrification medium containing (in

grams per litre) 0.504 NaHCO₃ and 0.265 (NH₄)₂SO₄. For dry weight determination the sludge was dried at 100 - 105 °C for 24 h. Total phosphorus was quantified by the vanadomolybdophosphoric acid colorimetric method after persulfate digestion, according to APHA (1985) [14].

In laboratory the sludge was fed with a medium containing (in g/l) 0.32 NH₄Cl, 0.6 MgSO₄·7 H₂O, 0.07 CaCl₂·2 H₂O, 0.1 EDTA and 2 ml of trace metal solution containing 1.5 FeCl₃·6 H₂O, 0.15 H₃BO₄, 0.03 CuSO₄·5 H₂O, 0.03 KJ, 0.12 MnCl₂·4 H₂O, 0.06 Na₂MoO₄·2 H₂O, 0.12 ZnSO₄·7 H₂O, 0.15 CoCl₂·6 H₂O [15] and 0.022 KH₂PO₄.

Results and discussion

The nitrification rates of the activated sludges from the Põlva and Viiratsi sewage plants are not high; up to 1.5 mg N/(g · h). The determination of the nitrification rates after different anoxic condition residence times (Viiratsi activated sludge) indicates of nitrification rates after short residence times. The maximal nitrification rate was observed after anoxic conditions residence time 2 - 3 h. The rate increase was ~20 %. After 4 - 5 h the preliminary rate was observed and after 20 h residence in anoxic conditions the nitrification rate was practically zero. As the short oxygen starvation increases the nitrification activity, the existing anaerobic zone in EBPR process can improve the following nitrification process in aerobic zone. A similar phenomenon was observed in polyphosphate synthesis, here switching off the O₂ supply increases polyphosphate kinase activity. Activation of enzyme system caused by oxygen starvation can be the reason for increase of nitrification activity too. The significant suppression of nitrification activity after long retention in anoxic conditions is in contradiction with some reported data and the through investigation is necessary here. The oxygen consumption rate during the raising of anoxic conditions was constant on the all DO concentrations to the minimal measured values (~0.03 mg/l). Still, the oxygen consumption is not only due to nitrification.

The activated sludges were obtained in winter, the air temperature was -5 °C, the sludge temperature was different parts of plant. The experiments were carried out and the sludge was retained at room temperature (~22 °C). On the first days of nitrification rate decreased abruptly, more than twice for three days. In the literature is mentioned that a rise in temperature of 10 °C gave about a three-fold rise in

nitrifiers growth rate [16] and here we have once more a contradiction with literature. It is possible that we have two different kinds of nitrifiers in our activated sludge, one of them is cryophilic, the other mesophilic. According to temperature one of them is dominant. In winter the cryophilic nitrifiers are dominant and the higher temperature is unacceptable for these microorganisms. The mesophilic microorganisms population is not enough numerous and the nitrification rate decreases. After some days the nitrification rate starts to increase, as the mesophilic bacteria become dominant.

In the Põlva sewage plant was observed the rise of activated sludge P content after a period of low DO concentration outside of aerators [13]. The high activated sludge P content is a feature of EBPR process. The necessary condition for the EBPR process is that the biomass passes through the anaerobic zone. In this zone polyphosphate-containing bacteria take up easily degradable organic matter, primarily acetate, and accumulate it as poly- β -hydroxybuturate (PHB) [17] or poly- β -hydroxyvalerate (PHV) [18]. Under aerobic conditions the polyphosphate-accumulating bacteria consume PHB/PHV for growth and accumulate polyphosphate. In the anaerobic zone not only the absence of DO is necessary but the absence of nitrates is necessary too. P is only removed satisfactorily in aerobic zone if a good P release in anaerobic zone has been obtained. The inhibition of anaerobic P release by nitrates occurs in the acetogenesis step. Several authors have observed P release in the presence of both nitrate and acetate. In the Põlva sewage plant average influent nitrate concentration is ~ 4 mg/l, but the recycle sludge nitrate concentration is more higher. It seems as if the EBPR mechanism arose despite the nitrate presence in the solution. Similar observations are reported for DO; P release can begin at low DO values, depending on sludge conditions [19]. At a limiting content of DO, P uptake would probably occur on the surface of sludge flocs, while in the interior P is released, as in the interior of sludge flocs the anaerobic conditions can exist. Nevertheless, without strict anaerobic conditions there can not be a good P release.

The enhanced activated sludge P content in Põlva sewage plant remained during four months. The P removal efficiency was not stable. Maximum efficiency was more than 90 % and effluent P content less than 1 mg/l, but in some days removal efficiency was less then 50 %. At the same time the sludge P content was rather stable, approximately 3.5 %. All this time there was not any anaerobic zone in the plant. In

the clarifier the DO concentration was low, but the nitrate concentration was high and there were obviously anoxic conditions. It seems as if the enhanced sludge P content can remain for a long time without existing the conditions for EBPR mechanism.

Conclusions

The results show that the short-time residence in anoxic conditions increases the rate of following nitrification in aerobic conditions, but after long-time residence in anoxic conditions the nitrification rate decreases significantly. After the abrupt temperature change the nitrification rate decreases too. It is possible that we have two different nitrifiers in our activated sludges - cryophilic and mesophilic ones. In the full-scale sewage plant the enhanced sludge P content remained for a long time after vanishing the conditions which seem to be necessary for EBPR mechanism operating.

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PROBLEMS OF MONITORING HYDROPHOBIC ORGANICS

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The design of many of the official USSR analytical methods for environmental monitoring, including those for air and water sampling, was found to be inadequate for generation of reliable analytical data. To demonstrate the design deficiencies, Soviet and international standard methods for the measurement of some hydrophobic organic pollutants, e.g. polycyclic aromatic hydrocarbons, chloroorganic compounds and petroleum hydrocarbons are described and discussed. The combination of outdated Soviet sampling procedures, obsolete equipment, the lack of use of blind samples, method blanks, and internal, external and surrogate standards has led to a situation in the USSR in which the hazard of pollutants in human environment cannot be evaluated.

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INVESTIGATION OF *FUNGI* IN INDOOR AIR AND CONTROL OF THEIR GROWTH IN LIBRARY REPOSITORIES

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A severe problem in libraries and archives is the biological damage to books and manuscripts, caused mostly by *filamentous fungi*. Microorganisms, including *filamentous fungi*, enter book repositories with outdoor air, incoming books, equipment and people. The main source of book contamination with fungal spores is the surrounding air. Nowadays more than 300 species of *filamentous fungi*, deteriorating books and manuscripts are known. *Filamentous fungi* decompose micro- and macrostructure of paper and other materials of books, such as leather, parchment, textiles, adhesives and dyes.

Storage conditions in Tartu University Library have been far from normal. Formerly library stocks were accommodated in several buildings where unsuitable heating conditions caused strong fluctuations in relative humidity (10...95%); ventilation was practically lacking; both uncleaned and disinfected books were kept in the same repositories. Storage conditions improved considerably in 1981 when the library was transferred to a new air-conditioned building. However, the danger of microbiological deterioration still exists. A great part of the stocks has been kept, during a shorter or longer period, in conditions favourable for the development of *filamentous fungi*; in spite of disinfection, they may be contaminated by the *fungal mycelium* and spores. The present air-conditioning devices are not able to provide a stable microclimate all the year round. There occur great differences in relative humidity in summer and winter months: 55... 80% and 37...50% respectively.

In this study the usefulness of microbe composition of air samples as an indicator of a mold problem was studied in the repositories of Tartu University Library. Microbiological analyses were carried out since May 1991. The air samples were taken with a Krotov impaction air sampler on the surface of a sterile solid medium. Media with a diffe-

rent composition (the mixture of fishpeptone and malt agar; the modifications of Czapek-Dox medium, to which carboxymethylcellulose or milk were added as a source of carbon) were used. The volume of filtrated air was 50 - 100 litres, depending on the degree of the microbiological contamination of repositories. The following microbiological characteristics were determined from the tests: the total number of microorganisms, the total number of fungal spores and the total number of spores of *filamentous fungi* with cellulolytic and proteolytic activity. The number of colony forming units (cfu) was expressed per 1 m³ of the air. The sampling height was 1.5 m.

From the point of view of the biological damage of storage items, the microbial number and the composition of microflora in repositories are the most important characteristics. On the basis of the data obtained it can be said that *filamentous fungi* and their spores are permanently present in all the repositories studied - A, B, C and the Department of Manuscripts and Rare Books.

The C repository is the most heavily contaminated. High concentration of airborne microorganisms (1000... 2400 cfu/m³) and fungal spores (400...1200 cfu/m³) were found in the air of C repository. In C repository the number of fungal spores varies greatly depending on the period of test taking. This suggest a permanent source of contamination. The C repository lies deepest from the ground level on the second basement floor. Due to badly isolated outer walls relative humidity there is 5-15% higher than in other repositories. As a result of permanent moisture on the corridor walls, *mycelium* is growing on them which, in its turn, causes the secondary contamination of the air by spores and *mycelium* fragments. Airborne fungal spore counts do not necessarily reveal exceptional fungal growth in buildings, because exposure to high spore counts is also associated with certain situations, changes of environmental conditions, frost-free periods or some human activities. Thus, visible investigation in a building is as important as air sampling. Particularly, in the case of suspected microbial contamination on indoor surfaces, air sampling is not needed if microbial growth can be certified from contaminated material by means of surface sampling. Contaminated materials should be removed, and if this is not possible, they should be cleaned and dried carefully.

Episodic contamination by microorganisms (maximum peaks varied from 800 to 1600 cu/m³) in the B repository can be explained by

special features of ventilation. Results of the sampling showed fungal spores concentrations ranging from not detectable to 850 cfu/m³.

In the A repository the latest publications are kept and most lendings are made from there. The initial data of the observation period show that the microbiological state of the A repository was the best. The latest findings, however, reveal growth in the number of microorganisms and fungal spores in this repository. Viable counts of microorganisms (800 - 1300 cfu/m³) and fungal spores (400 - 500 cfu/m³) in the air of A repository may be caused by the humid winter of recent year and irregular heating. The difference between the highest and lowest relative humidities in the A repository is ~30%.

The most stable micro- and mycoflora occurs in the Department of Manuscripts and Rare Books. Older, often mould damaged books and manuscripts are kept there. The maximum concentration of airborne microorganisms was under 4000 cfu/m³ and the number of fungal spores was under 400 cfu/m³. Stable proteolytic microflora occurs only in this repository, which can be explained by the special composition of the materials (containing leather and parchment) kept there. However, the influence of the potential contamination sources has been stabilized by very intensive ventilation.

Conclusions

1. *Filamentous fungi* are permanently present in all library repositories. In repositories, the main fungal spore sources are outdoor air, dust and contaminated storage items.

2. Indoor air fungal spore counts varied considerably from repository to repository and even within the same repository. Differences in spore counts between repositories are mostly caused by different heating and ventilation systems and construction practice.

3. In the repositories of Tartu University Library the number of fungal spores in 1 m³ air is within the allowed limits. On the average, there occurs 200 - 250 spores per 1 m³ in the repository. Although there are considerably fluctuations, there is no pronounced seasonal pattern of change in fungal cfu number. Episodically the air in the repositories contains sufficiently high fungal cfu levels.

4. Counts of fungal cfu are generally lower than corresponding bacterial counts. In repositories the percentage count of fungal cfu comprised 10 - 50% of the total airborne microflora count respectively.

5. The number of microorganisms and fungi in the repository air depends on the following factors: temperature and humidity conditions; the direct influence of ventilation system and outdoor air; the character of materials kept in the repository; special features of work (cleaning).

6. The mycoflora in the air largely corresponded to the fungal flora on surfaces (walls, backs of the books) in the respective repository.

7. The present study showed that building materials become easily mouldy if sufficient moisture is available on a surface for a short time (the C repository). Thus, control of moisture conditions in a building is the best way to prevent microbial problems.

8. Permanent microbiological monitoring of the air, particularly with respect to the number of fungal cfu, provides information on conditions in the repositories and helps to avoid the potential biological damage of storage items. We suggest the airborne microbiological parameters as very sensitive for assessment of the ecological state of the repository air.

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EVALUATION OF SEDIMENT POLLUTION DATA: EXAMPLES FROM THE GULF OF RIGA-STATUS AUGUST 1995

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Summary

Most of heavy metals and organic pollutants are associated with organic matter, clay surfaces, sulphides and or iron manganese hydroxides which preferably are deposited with fine grained sediment components. The distribution of sediment types on the seafloor is therefore essential for the understanding of the transport and distribution of heavy metals and nutrients on the seafloor, and the sediments is the ultimate sink for most elements.

The sediment distribution on the seafloor in the Gulf of Riga has been mapped by high resolution seismics and sampling. Accumulation areas and non accumulation areas have been identified. Sediment budes has been made based on maps of the thickness of the marine sediments. On an average over 7800 years the annual deposition in the mud accumulation basins is estimated at 1.3 mill ton dry material per year, or 285 g/m²/yr on ca 30 % of the Gulf area. Today the rivers supply ca 0.7 mill t. In addition huge quantities of sand has been transported into the Gulf from south and has been deposited on the southern shore of the Irben Strait. A characteristic feature of the Gulf is the extensive areas (50 - 70%) with early Holocene sediments almost in the seafloor proving that on an average no net deposition takes place here. Seismic profiles show that glacial clays and postglacial clays older that the marine has been eroded extensively on the seafloor- so internal erosion of the seafloor and coasts are probably an important sources natural for sediment matter, nutrients and metal in addition to the rivers. The recent deposition in accumulation was studied on 16 selected sites and the recent accumulation rate determined by Pb 210 dating supplied with

Cs 137. The local accumulation rate was very high; 0.5 - 2 kg dry matter/m²/yr or 2 - 9 mm/yr. Bioturbation is often low in the accumulation areas because the benthic fauna in the mud is so impoverished by the brackish water. The combined with high accumulation rates of muddy sediment offer excellent condition for recording of the pollution of the seafloor with heavy metals through time, and for sensitive sediment monitoring of changes of fluxes.

Coresamples from 13 of the depositional sites in the Gulf of Riga have been analysed for their content of heavy metals down to ca 25 cm below seafloor. Earlier results from the Gulf of Riga have been compiled and their quality assessed. 50 surface samples from north of 58 N, mostly in non depositional areas have been analysed for Fe, Mn, Cu, Pb and Zn. From these investigations it can be concluded that:

- The concentrations found is generally low to moderate and comparable to those found in the rest of the Baltic Sea. Moderately elevated concentrations have been observed locally near shore mud areas in the northern Gulf.

- This conclusion is in agreement what has earlier been published, although the assessment of the quality of the analysis revealed problems with the analysis of some of the metals, especially for Hg and Cd in low level concentrations. (>1 ppm)

- There has been an increase in the concentration levels in the surface sediments compared to the pre-industry background by a factor 3 - 7 for Mercury, 2 - 8 for Cadmium and 1.5 - 3 for lead.

Participating institutions in the project: Heavy metals in the Gulf of Riga Project.

Geological Survey of Denmark (co-ordinator- Birger Larsen)

National Environmental Research Institute, Denmark (Britta Petersen)

The Water Quality Institute, Denmark (Arne Jensen)

State Company Latvia Geologija, Latvia (Janis Prols, Oskars Stiebrins)

Institute of Biology, Latvian Academy of Science, Latvia (Zinta Seisuma)

Geological Survey of Estonia, Estonia (Rein Raudsepp, Valter Petersell, Jaan Kask, Maire Sakson)

Background

Most heavy metals are associated with organic matter, clay surfaces, sulphides and or iron manganese hydroxides which preferably

are deposited with fine grained sediment components. The concentration of the heavy metals on a dry weigh basis is consequently much higher in mud sediments than in the sand sediments from the same general area. The distribution of sediment types on the seafloor is therefore essential for the understanding of the transport and distribution of heavy metals and nutrients on the seafloor. Sediment maps also serve as base for planning of sampling points.

The basic technique is to combine marine geological mapping of sedimentary environments (erosion, depositional areas etc.), measurements of regional sedimentation rate based on geophysical data and knowledge of the geological history of the area supported with measurements of local mixing rates and sedimentation rates by Pb 210 profiles. The quantitative description of sedimentary processes and sedimentation pattern in the Gulf of Riga will provide basic data for several of the other studies planned for the area on pollution budgets and turnover of nutrients.

The time-model will be used for the assessment of the sensitivity of sediment monitoring stations and forecast of the development in sediment concentrations in response to changes in the input of pollutants.

Objectives of group 5d:

- To clarify the role of the bottom sediments and sedimentation processes in Riga Bay for the area distribution and vertical distribution in the bottom of inorganic pollutants such as selected heavy metal (Hg, Cd, Pb, Cu and additional, if local problems are identified).
- To establish a quantitative understanding of the sedimentation in the Bay of Riga (a sediment budget) as a contribution to an overall mass-balance of selected substances. The mass balance describe the relative importance of individual sources (outfalls, river inputs atmospheric input, sediment erosion/net deposition, sediment exchange and water exchange).
- Attempt to establish the history of regional pollution with metals through time from selected sediment cores and other time series.
- Based on modelling of the mixing processes, asses the suitability of selected sediment stations in future monitoring and attempt to forecast the effect in sediment concentration of changing the input of heavy metals to the Bay.

Marinegeological mapping and Sediment budget

In co-operation between the Geological Survey of Estonia and the state company "Latvijas Geologija" now the Geological Survey of Latvia in Riga maps in 1:200 000 covering the whole Gulf of Riga have been produced with the following themes: Bottom sediments, Sedimentation conditions, thickness of Littorina and Postlittorina muds, Bathymetry. The maps south of 58 °N has been compiled from by the Geological Survey of Latvia based on previous confidential maps based on extensive sampling and seismic data in that organisation. Comparatively few data existed north of 58 °N (Lutt and Raukas 1993) so in 1993 the Geological Survey of Estonia carried out an marinegeological investigation as a contribution to the Gulf of Riga Project. The maps are described in a preliminary report: "Sediments in the Gulf of Riga". For the area south of 58 °N also a map of the fine grain fraction > 0.005 mm and the content of organic matter has been compiled.

Using the samples and the seismic sections it has been possible to differentiate deposit from non-deposit areas, where older deposits are found often less than 10 cm below the seafloor (Figure 1). An extensive continuous accumulation area is found in the southern parts and east of Ruhnu, while the area west of Ruhnu is characterised by a complicated morphology with many small accumulation areas with intervening non deposit areas. The northern part is mostly slow or non-depositional bottoms. Erosional unconformities on top of the older Baltic deposits suggest that erosion of older late Quaternary deposits in the seafloor has occurred. The base of the marine mud is often a fairly good acoustic reflector that can be observed by special echo sounders, examples are shown on Figure 2.

Regional accumulation rates-a geological approach

An estimate of the regional mean rate of accumulation of dry matter in the muddy (fine grained) has been estimated based on:

- A seismic mapping of the thickness of marine sediments and areal extension in the Gulf of Riga.

The area is defined by the coastline and the longitude of the southern point of Saaremaa (22° 03' E) and to the North of (58° 33'N).

- An estimate of the variation of the content of dry matter in the sediment with depth.

- An estimate of the starting time for marine sedimentation in the area.

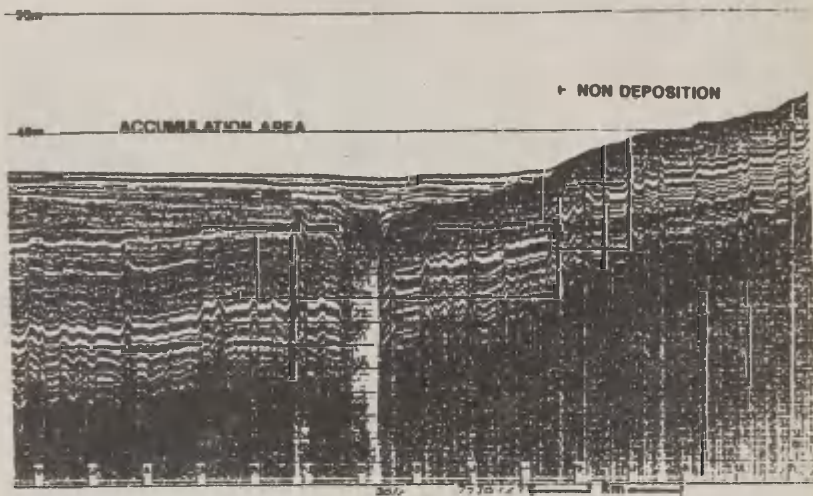


Figure 2. Seismic profile south of Ruhnu showing the difference between accumulation basin and non deposition or very slow deposition.

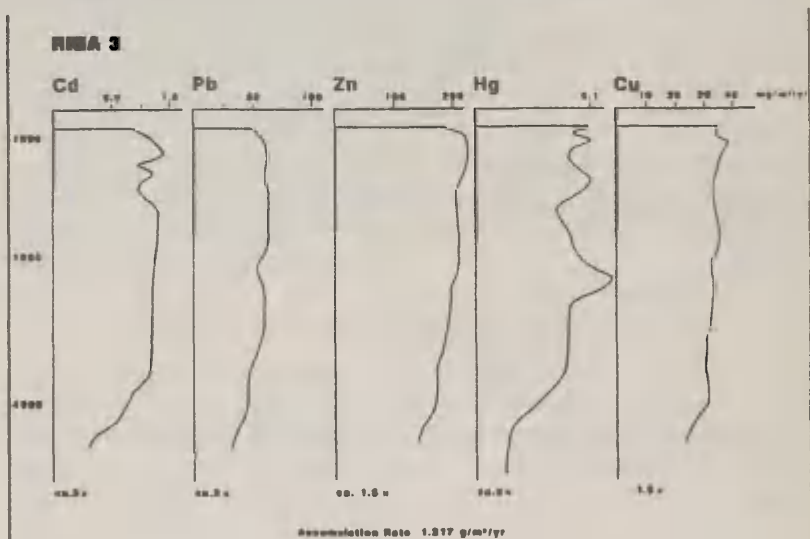


Figure 3. Accumulation rates of heavy metals through time. Based on accumulation rate of sediment from Pb210 and metal concentrations. Presumes no movements of metals since deposition.

The Gulf of Riga as other parts of the Baltic Sea were invaded by the sea about 7800 - 7200 years ago (Kessel and Raukas, 1979, Veinbergs 1979) and marine conditions established. The water level in the late fresh Ancylus lake which preceded the Litorina Sea stage was not far from the present sealevel (Kessel and Raukas 1979, Veinbergs 1979) so the change into marine condition probably took place by gradual intrusion of saltwater without major changes in the dynamics of sedimentary conditions except in shallow coastal areas.

Table 1. Thickness of muddy sediments in the Gulf of Riga east of 22° 03'

Thickness	0 - 2 m, 1308 km ²
	2 - 4 m, 1560 km ²
	4 - 6 m, 776 km ²
	6 - 8 m, 501 km ²
	8 - 10 m, 192 km ²
	10 - 12 m, 129 km ²
	12 - 14 m, 70 km ²
total mud depositional area	4536 km ² ca 30 % of area
the sand deposit areas are estimated at	1679 km ²
non deposit + sand deposits	12441 km ²

To estimate the amount of dry matter the following tentative assumptions have been made, based on experiences from the Lillebalt area:

Watercontent % of dry matter = $250 + 125 \log D$ in meters where D is thickness of mud in m.

Dry density of dry matter is 2.55 t/m³. Based on this it is estimated that 10⁹ t of dry matter have accumulated in the mud areas. This is deposited since the ingresson of the Litorina Sea 7800 - 7200 years ago. The mean annual deposition is thus $109/7800 = 1.3 \cdot 10^6$ t/yr or on an average over 7800 years 285 g/m²/yr in the mud accumulation areas.

According to Pustelinkov (1992) is the annual deposition in the Gulf of Riga $1.9 \cdot 10^6$ t of which half is deposited in the nearshore areas and thus include the huge amounts of sand which is brought into the Gulf along the west coast of Latvia and partly deposited along the northern shore of the Kolka area. According to Pustelinkov (1992) about $0.74 \cdot 10^6$ t/yr dry matter, of which $0.1 \cdot 10^6$ t is organic matter and a simi-

lar amount is silica is supplied to the Gulf from the rivers. As a very rough guess about 10 % of the marine sediment is organic matter, diatom shells, carbonate and sulphur in sulphides and other autochthonous components produced in the Sea, corresponding to $0.2 \cdot 10^6$ t. From the seismic evidence it is certain that a substantial erosion of older pre-marine sediments have taken place in the seafloor and the coastas. An other source is sediment transport into the Gulf of Riga from the Baltic. Based on the coastal development (Knaps 1979) and the distribution of suspended material in the near shored zone (summarised for the project in Pustelnikov 1995) it is suggested that this is an important source for sandy sediments and presumably also for suspended material. This need further investigations.

Recent sedimentation

Sampling

The recent deposition in accumulation areas was studied on 16 selected sites and the recent accumulation rate determined by Pb 210 dating supplied with Cs 137 in cooperation with the Finnish Institute of Marine Research on "R/V Aranda" 1993 - 1994 (Larsen and Jensen 1995).

The uppermost 25 - 50 cm of the seabed was using a Gemini double corer and sampled in 1 cm slices. 3 sets of samples were collected and frozen. Also samples for organic contaminants was taken for Dag Bromann. Detailed seismic records (12 kHz) were obtained between and across the sampling stations, in total 840 line km in the Gulf of Riga.

The Geological Survey of Estonia has within the project made additional sampling north of 58° N and the Pärnu River estuary and along the southern coast of Saaremaa (Kask and Sakson 1994).

Pb 210 and Cs 137 dating.

The accumulation rate of sediment matter and intensity of bioturbation was estimated using Pb 210 for all 16 sites and supported by Cs 137 for 5 of the cores. The results has been reported in (Larsen and Jensen 1995). Of the 16 the 11 seem to be nearly undisturbed or moderately disturbed and promising for detailed studies, while the rest are strongly disturbed. The local accumulation rates were very high;

0.5 - 2 kg dry matter/m²/yr or 2 -9 mm/yr, this is slightly higher than previously determined (Kuptsov et al 1984). Bioturbation seems often to be low in the accumulation areas because the benthic fauna in the mud is so impoverished by the brackish water. This combined with high accumulation rates of muddy sediment offer excellent conditions for recording of the pollution of the seafloor with heavy metals through time, and for sensitive sediment monitoring of changes of fluxes. In the 11 stations net deposition rates of nutrients, organic matter and trace metals will be available early soon.

When slicing the sediments a worm *Marenzelleria viridis* newly introduced to the Gulf was found even below 20 cm. It is thus possible that deeper bioturbation will change the conditions for sediment monitoring in the future.

Chemical analysis

In the metal analysis made on the cores for the project total concentration (Hf for PIXE) and extraction with strong acid (1:1 HNO₃) of Hg, Cd, Pb, Zn and Cu and in some cores also other elements has been measured; in order to make comparable results (Perttilä and Brüggmann 1992). Analysis was carried out from the labs at DMU and FIMR, both with well developed quality control. For comparison some samples were also analysed at the laboratory of Zinta Seisuma - using normal practice. Problems with Hg and Cd at low concentrations and Cu were identified.

The chemical data is summarised in Petersen et al 1995, but has not been evaluated yet but the following tentative conclusions appear:

- The concentrations found are generally low to moderate and comparable to those found in the rest of the Baltic Sea. Moderately elevated concentrations have been observed locally nearshore mud areas in the northern Gulf.
- This conclusion is in agreement with what has earlier been published, although the assessment of the quality of the analysis revealed problems with the analysis of some of the metals, especially for Hg and Cd in low level concentrations (>1 ppm).
- There has been an increase in the concentration levels in the surface sediments compared to the pre-industry background by a factor 3 - 7 for Mercury, 2 - 8 for Cadmium and 1.5 - 3 for lead.

PIXE analysis for 24 elements has been performed on the two dated samples from 1993 and top and bottom sample on most of the

cores. Some results recalculated to a flux through time are shown on Figure 3. The preliminary calculation indicates that the pollution with Cd, Pb, Zn and Hg started in the central Gulf of Riga about 1900 and according to this method has remained fairly stable since 1920. The increase in flux about 2 to 4 times the background, which is about what we find in Danish waters but the elevated fluxes seems to be developed earlier in the Gulf of Riga. this has to be verified by further studies.

Semiquantitative spectroscopic analysis has been made for 35 elements on 118 samples from the area north of 58° N by EGS. Based on this combined with inspection and grain size analysis about 50 samples was selected for quantitative analysed for Cu, Zn, Pb, Fe, Mn (Kask and Sakson 1994). Hg and Cd will be made in 1995. Many samples are from non-deposit bottom areas with is characterised by precipitation of Fe-Mn nodules. The concentrations found is generally low to moderate and comparable to those found in the rest of the Baltic Sea. Moderately elevated concentrations have been observed locally nearshore mud areas. The importance of these widespread areas for the exchange of metals has to be clarified. High phosphorous contents have been noted at some of these sites.

Compilation of heavy metal data from the Gulf and its surrounding

Data on the metal and nutrient input from rivers and downfall has been collected. The Latvian river data has been compiled in (Andrushaltis et al 1993), (Kask and Sakson 1994) contains a compilation of input of nutrients and metals (river, atmospheric) from Estonian territory. As a completion to the Estonian network of measuring stations for dry and wet atmospheric deposition a new sampling station has been established on Ruhnu Island situated in the middle of the Gulf, in August 1994. New Estonian downfall data (dissolved N, P, F, Cu, Zn, Pb, Cd) including 1 quarter of 1995 has been reported by Petersell (letter 1995), the composition of the dry downfall will be available in 1995. Sampling and determination of metals in rivers the Estonian (Petersell-Keis) and Latvian (Seisuma and Legzdina in prep.) has been continued. The concentrations of all heavy metals studied in the mouth of river Daugava are significantly higher than in the water inland from Riga indicating the influence of Riga - however a clear decrease in the concentrations of Cu, Cd, Pb, and Zn has been observed from 1989 to 1991 (Seisuma et al 1993, Seisuma and Legzdina 1994). The 1994 figures is not available yet. We suppose that it is possible to make a reason-

able mass balance for some of the heavy metals for the Gulf of Riga, but this has been postponed to 1996.

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* **Marked with bold** are reports produced in the period 1993-1995 mostly as base for the work within the heavy metal group. Some of the reports have been distributed within the Gulf of Riga Project. None of the reports are formal publications which can be cited without the permission of the authors.

SEDIMENTS AND SEDIMENTATION IN THE BALTIC SEA

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The Baltic Sea offers an opportunity to study sediments in very precise ways. The reason is that the sedimentation is very rapid and annual layers in the sediment basins are formed. Compared with the world oceans where the rate of sedimentation on the sea floor is some millimeters in 1000 years, the Baltic Sea sedimentation is in several places of the order of a few millimeters per year.

The temporarily anoxic environment effectively prevents any higher life from colonisation of the sea floor. This is seen in undisturbed layer by layer sedimentation where no bioturbation has occurred. These undisturbed sediments are found mainly in the Gotland Deep area, but temporarily also in the Gulf of Finland and the Bornholm Basin. This type of sediments form an interesting *history book* where the pages can be interpreted by using modern analytical methods. The recent development of different dating methods have made it possible even to give numbers to the *pages*.

Several anthropogenic elements and components are found in the sediments for the first time in the geological history and the datings clearly show the time of the start of using them. Such man made elements in the sediments are DDT, PCB, and a couple of radionuclides.

By reading the history book back in time it is possible to establish views of the state of the Baltic Sea before influence of Man has changed the general circumstances. A slow eutrofication - even of the open Baltic Sea - has evidently taken place. This is seen in the surface sediments as increasing contents of organic matter. Organic matter is an important agent in scavenging heavy metals from the water to the sediments. As a result of increased sedimentation of the organic component some heavy metal concentrations have increased even 5 to 20 times compared with the past.

During the recent years, as a result of the *salt pulse* 1993, many anoxic bottom areas have been oxidised and benthic fauna is recolonizing the deep areas, even the Gotland Deep. There is a risk that these animals will meet too high concentrations of harmful substances when they live on bottoms which have been very active in sequestering organic matter and metals. A risk of recycling is evident.

DETERMINATION OF THE INFLUENCE OF SURFACTANTS TO OXYGEN PERMEABILITY THROUGH GAS-LIQUID INTERFACE

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The exchange of oxygen between the liquid and gas phases determines the stationary gas content in natural and artificial waterbodies where the oxidation of pollutants is constantly consuming oxygen in water. Gas exchange between the phases depends to a considerable extent on the state of the interfacial surface between liquid and gas. The adsorption of surface-active compounds in the gas-water boundary decreases the rate of oxygen mass transfer from the atmosphere to the hydrosphere and therefore the ability of natural waterbodies and water cleaning systems to decompose the pollutants is declining.

In our work we have investigated the influence of surface-active compounds on the permeability of oxygen through the gas-water surface. Special device with an oxygen analyzer was designed and methods to provide experiments were developed. The mathematical model was worked out to describe the kinetics of oxygen mass transfer. In parallel to the oxygen mass-transfer measurements, the surface tension values of all solutions under investigation were determined.

The experiments were carried out in the solutions containing the surface active components in the range of concentrations 0.0005 - 0.01%. Methanol, ethanol, 1-propanol, 2-propanol, butanol and pentanol were chosen as surfactants. The test solutions were deoxygenated by adding Na_2SO_3 .

The diffusional characteristics of the surface layer between gas and liquid were examined by the rate of escaping oxygen from small volume V upon deoxygenated solution under investigation by using the oxygen sensor. By adding the surface-active component to the test solution, the molecules of the surfactant adsorb to the gas-liquid interface and the permeability of the surface layer diminishes. This, in its turn, decreases the flow of the gas component (O_2) through the gas-liquid interface.

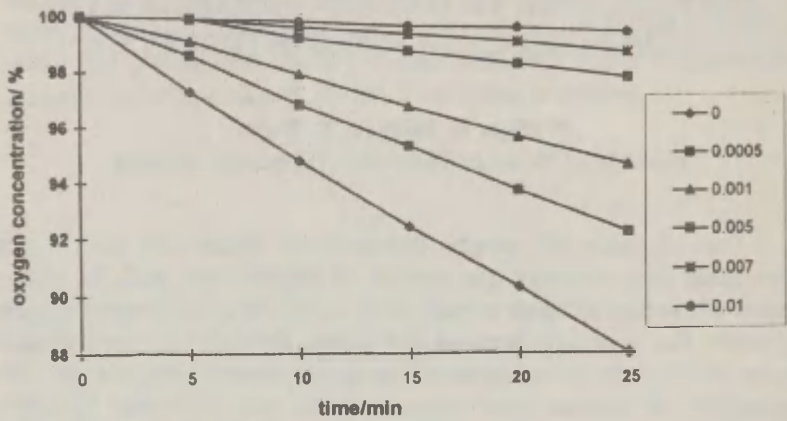


Figure 1. The time dependencies of oxygen concentration in gas volume V at the different concentrations of buthanol.

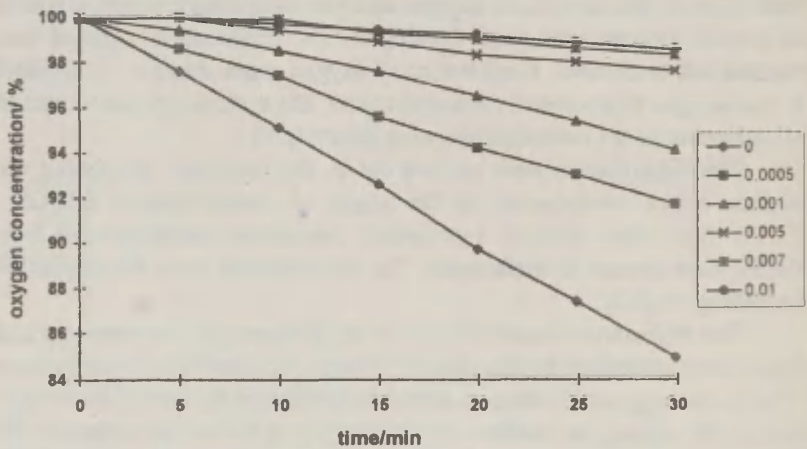


Figure 2. The time dependencies of oxygen concentration in gas volume V at the different concentrations of penthanol.

The time dependence of the decrease of the oxygen concentration in volume V is given in figures 1 and 2 for 1-butanol and 1-pentanol solutions. As is seen from the figures, the increase of the concentration of the surfactant in the solution causes the increase of the resistance of the surface layer to the oxygen flow through it. The increasing of the length of the hydrocarbon chain diminishes the solubility of the surfactant molecules and therefore the surface activity will arise. As it is seen from the figures, the surface permeability diminishes more intensively in the case of pentanol whose hydrocarbon chain is longer. Comparing the influence of 1- and 2-propanol, to the oxygen permeability of the gas-liquid interface shows that 1-propanol with straight chain has less influence on the gas transfer. 2-propanol covers a larger area of the surface and the probability of a gas molecule passing through the gas-liquid interface diminishes

The above described experimental results will be the basis for working out the analytical method for measuring the complex behaviour of the surfactants to the rate of gas permeation through the gas-liquid boundary. Oxygen exchange between the gas phase and water is especially important for wastewater cleaning systems, where the increasing of surfactant concentration in water decreases the rate of oxygen dissolution in water and therefore it needs more energy to maintain the desired oxygen level.

DETERMINATION OF PHENOL USING A *PSEUDOMONAS PUTIDA* CONTAINING BIOSENSOR

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Introccution

The large-scale processing of oil-shale in Estonia has resulted in a distribution of pollutants, e.g. phenolic compounds, into the environment. For instance, annually several hundreds tons of phenols are carried by the leachates from the solid waste landfill of oil-shale processing industry to the Baltic Sea [1]. Thus, the measurement of phenol is very essential for environmental control, but also for the development of the efficient wastewater treatment processes.

From the various analytical procedures for phenol determination in water samples, gas chromatography and spectrophotometry have been most widely used [2]. However, due to several advantages, including insensitivity to variations in optical properties of the sample, relatively low cost, potential to continuous monitoring, attempts have been made to develop whole-cell biosensor systems for the analysis of different phenolic compounds [3-6].

The present study is concerned with the properties of a phenol sensitive biosensor based on immobilized whole cells and a flow-calorimeter device.

Calorimetric biosensors have shown to give satisfactory results in many analytical fields, including biotechnology and environmental monitoring [7]. In the environmental control the calorimetric detection can be used in two different ways. In some cases, by using of an appropriate microorganisms it is possible to metabolically convert the

specific compound and measure the heat of the process. The alternative is to measure the inhibitory effect of specific pollutant [7].

In this study the attractive feature of bacteria *Pseudomonas putida* EST1412, the ability to utilize preferably phenol, has been used. The characteristics of a biosensor, based on the measurement of metabolic heat from the bioconversion of phenol by immobilized cells by a flow-calorimeter device, is described.

Experimental

The bacterium *Pseudomonas putida* EST1412, provided by Dr. Maia Kivisaar (University of Tartu, Estonia), was selected for the study as the preferred phenol degrading organisms. Cells were cultivated at 30 °C in mineral culture medium with phenol at 5 mM as the sole carbon source.

Microorganisms were collected at exponential grow phase by centrifugation at 5000 rpm for 5 minutes in a SS-34 rotor (Sorvell, USA). Cells were washed twice with 0.9 % saline and were then suspended in 1 ml of the same solution. The obtained bacterial suspension was mixed 4 ml of sodium alginate. The final mixtures had cell concentrations of 0.005 - 0.015 mg dry weight per mg gel solution and the alginate concentration 2 % (w/v).

The sodium alginate-bacterial mixture was added dropwise into 100 mM CaCl_2 where alginate was crosslinked with Ca^{2+} -ions. The formed alginate beads were transferred to 0.05 M Tris-HCl buffer in 10 mM CaCl_2 (pH = 7.0). The beads had diameters ranging from approximately 1 to 1.5 mm and were packed into a small column in the flow-calorimeter device. When not in use, the immobilized cells were stored in buffer at 4 °C.

The flow-calorimeter system used has been described elsewhere [7]. A peristaltic pump was applied to produce a continuous flow of 0.05 M Tris-HCl buffer with 0.5 ml/min. The liquid was temperature controlled by passage through a heat exchanger at 30 °C before entering the column containing immobilized cells. At the outlet from the column a thermistor was registering the temperature of the liquid. The temperature increases in the flow-calorimeter produced by pulses of 0.2 ml of samples containing phenol were registered as peaks. The areas under the peaks or peak heights were measured as the responses of the developed phenol assay.

Results and discussion

The responses of the flow-calorimeter system to phenol measured as areas under peaks or peak heights respectively are shown in Figure 1. Both calibration curves illustrated in Figure 1 showed a good linearity up to 0.2 mM as shown in detail in Figure 2 and Figure 3. The upper detection limit may be due to an oxygen deficiency. It was possible to detect phenol down to approximately 1 μM . This detection limit was probably governed by the sensitivity of the bacteria used in the experiments. The sensitivity was in the same range as that observed for most enzyme based biosensors for a wide range of substrates.

With the conditions described above the capacity of the system was 4-8 samples per hour depending on phenol concentration in the tested sample.

The standard deviation was approximately 3% when 8 repeated pulses of 0.08 mM phenol were measured as peak heights during 8 hours. Since the response of the biosensor decreased in time it was necessary to calibrate the sensor every day in operation.

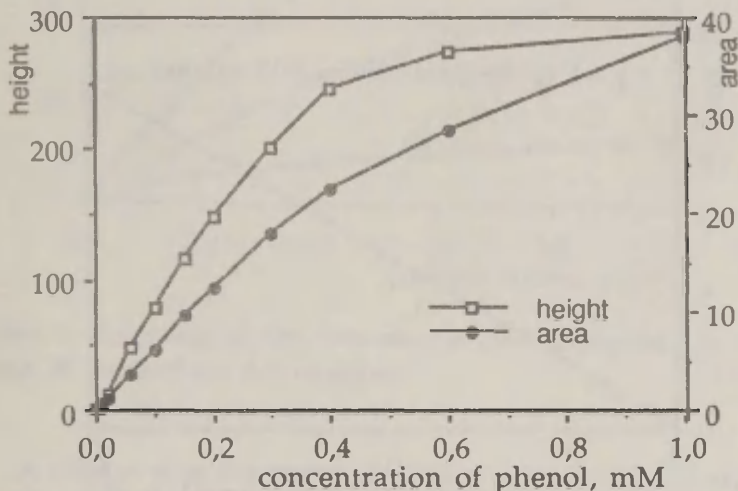


Figure 1. Responses from the *Pseudomonas putida* biosensor for different phenol concentrations measured as \square - peak heights or \bullet - areas under the peaks.

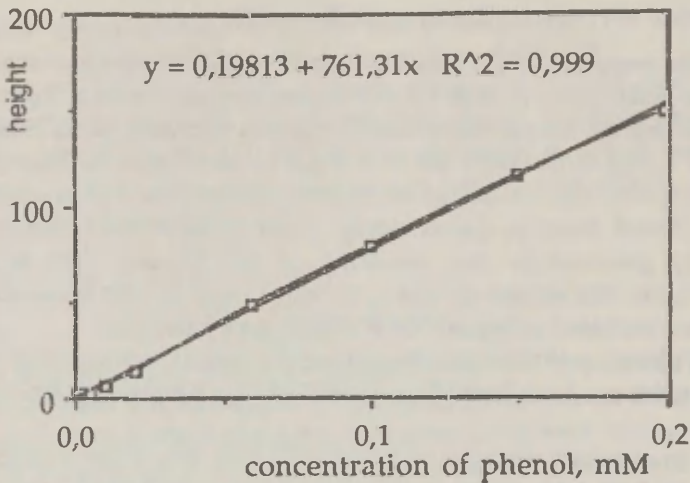


Figure 2. The linear range of the response of the biosensor to phenol measured as peak heights.

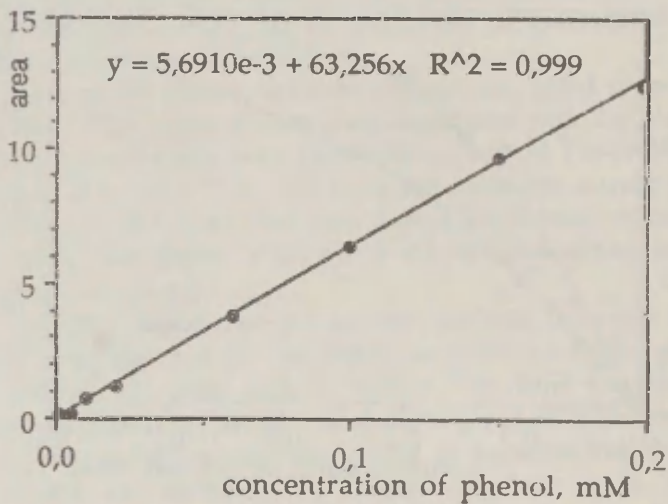


Figure 3. The linear range of the response of the biosensor to phenol measured as areas under the peaks.

Metabolic responses to catechol and resorcinol of immobilized *Pseudomonas putida* EST1412 cells grown on phenol were measured. Figure 4 shows response curves of the biosensor to phenol, catechol and resorcinol. It is obvious that resorcinol is a poor substrate to the cells. As can be seen from Figure 4 the sensor response to catechol was relatively high at higher concentrations. With the actual biosensor arrangement it was not possible to detect responses to catechol at concentrations lower than 0.03 M. Some sensitivity to catechol of this biosensor is unavoidable, since the first step in the oxidation of phenol is the formation of catechol, which is further processed by a 1,2-dioxygenase.

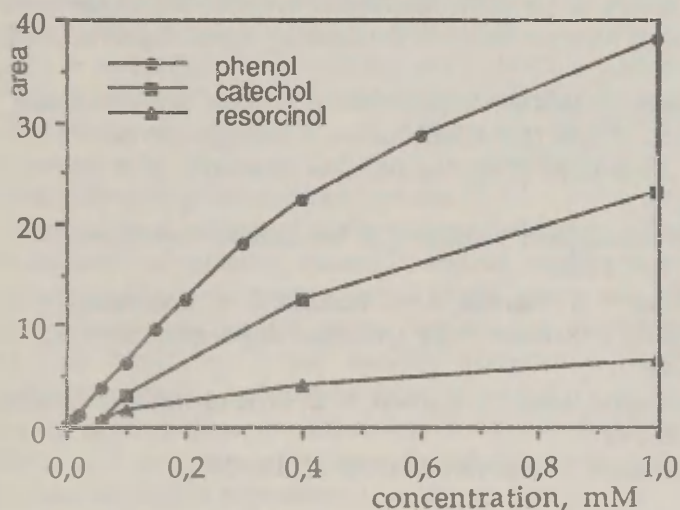


Figure 4. Responses of the *Pseudomonas putida* biosensor to • - phenol, ■- catechol and ▲ - resorcinol.

A range of other compounds, considered as potential substrates to the cells, were also tested to examine the specificity of the bacteria used in the biosensor. Responses to glucose, benzoate, salicylate, cresols and 2-methylresorcinol at concentration 1 mM were less than 3% compared with that from phenol. The absence of the sensitivity to alkylaromatics

can be explained by the inactive metacleavage pathway in the used bacterial strain.

The results show that the ability of *Pseudomonas putida* EST1412 to utilize phenol makes it suitable for the use in biosensors for phenol determination. The use of biosensors based on cells that also may be the main actors in the detoxification process is a new strategy for the future.

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POLAROGRAPHY AND STRIPPING VOLTAMMETRY OF SOME METAL- POLYELECTROLYTE COMPLEXES

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Voltammetric techniques have often been used to determine a content of heavy metals in natural waters. Besides the very low detection limit of the metal ions, the method has an additional advantage - a possibility to investigate the distribution of the metal ions among the "free" and "complexed" forms. Usually different species of metal are toxic in different way and quantity, of different the knowledge of the metal speciation is also essential to the understanding of many practicable properties of natural water systems [1].

Processes in natural waters like formation of complexes, adsorption on colloids and sedimentation, essentially depend on the pH, salinity, redox potential ect. In the present work a model system was analysed and the influence of the pH of the solution on the fraction of uncomplexed ("free") metal was studied. Polycarboxylic acids like polymethacrylic (PMA) and polyacrylic acids (PAA) were used as complexing agents because several classes of natural ligands (humic- and fulvic acid) are macromoleculare polyelectrolytes and weak acids, too, like homofunctional polycarboxylic acids.

The fraction of uncomplexed metal was found from the values of the stability constant of the metal - polycarboxylate system. The values of the stability constants were determined using voltammetric techniques. When formation and association processes of the complex are quick in comparison with diffusion processes, the complex is said to be electrochemically labile. In this case the normalized current ϕ of the metal ions is defined as

$$\phi = I_{\text{with ligand}}/I_{\text{without ligand}} = (1 + \epsilon K C_L)^p / (1 + K C_L)^p \quad (1)$$

where K is the stability constant ($K = c_{ML}/c_M c_L$), $\varepsilon = D_{ML}/D_M$ and the parameter p depends on the hydrodynamic conditions and is expected to be in the range between 1/2 and 2/3.

It must be emphasised that equation (1) is valid only if a 1:1 complex is formed and there must be a large excess of ligand over the metal ions [2]. Of course, as it was said previously, the complex must be electrochemically labile.

The complex formation of Zn^{2+} , Mn^{2+} , Pb^{2+} , Cu^{2+} and Tl^+ by the model polyelectrolyte PAA was studied. In all cases except for Tl^+ - polycarboxylate system, a decrease in the peak height, corresponding to decrease of the "free" metal concentration was observed when an excess of ligand was increased. Due to the association of metal ions with the polyacid, ϕ decreases and reaches a certain plateau value. This is a clear indication of the lability of the metal - polyelectrolyte system. The complexation curves were analysed in terms of a stability constant according to equation (1). We did not notice any complexation between Tl^+ and polyacid and, therefore, the fraction of uncomplexed metal was the main one in the solution. In case of the other studied metal - polycarboxylate systems the formation constants as well as the fraction of uncomplexed metal were strongly affected by pH of the solution. It was shown that there exists a linear dependence between pH of the solution and logarithm of the stability constant. Increasing pH causes increase of the degree of neutralisation of the -COOH groups, the polymer electric charge and, therefore, the energy of electrostatic attraction between metal ions and ligands. This results an increase in both, the fraction of complexed Me^{2+} and the equilibrium constant.

In Zn - PAA system $\log K$ values arise from $\log K = 3.28$ (pH = 3.9) to 4.24 (pH = 8.2) in 0.1 M KNO_3 . That corresponds to the decrease of uncomplexed zinc fraction from 55.9 % to 12,56 %. In Mn - PAA system $\log K$ values arise from $\log K = 4.19$ (pH = 4.8) to 5.14 (pH = 8.2) in 0.01 M CH_3COONa .

The fraction of uncomplexed Mn^{2+} decreases in the same region of the pH from 13.5 % to 1.36 %. For Cu - PAA system the uncomplexed metal content decreases from 28 % (pH = 4.2) to 0.6 % (pH = 6.0) and for Pb - PAA system from 20.6% (pH = 4.0) to 0.7 % (pH = 5.2). The results are presented in Table 1.

According to these results an essential part of metal ions will get rid of polycarboxylate complexes when to acidify the solution. In natural waters this have an importance, too, but there the situation is much

more complicated because of compete processes between all cations. Really the part of uncomplexed heavy metals surely depends on both, pH of the water and content of the other metal ions and ligands.

Table 1. Formation constants and fractions of uncomplexed metal of Me - PAA complexes at different pH values.

pH	Zn - PAA 0.1 M KNO ₃		Mn - PAA 0.01 M CH ₃ COONa		Cu - PAA 0.01 M KNO ₃		Pb - PAA 0.01 M KNO ₃	
	log K	Zn ²⁺ %	log K	Mn ²⁺ %	log K	Cu ²⁺ %	log K	Pb ²⁺ %
4.0	3.2	54.7	3.86	21.6	3.49	39.0	3.91	19.7
4.5	3.3	48.3	4.01	16.2	3.98	17.4	4.58	5.05
5.0	3.4	42.1	4.17	11.9	4.46	6.5	5.24	1.1
5.5	3.55	36.1	4.33	8.6	4.94	2.2	5.91	0.25
6.0	3.7	30.4	5.43	6.2	5.43	0.7	6.75	0.05

As so as natural water usually contains in a big excess of mono- and bivalent cations like Na⁺, K⁺, Ca²⁺, Mg²⁺ over the heavy metals, there was studied the influence of K⁺ and Ca²⁺ on the fraction of uncomplexed zinc ions. Results are presented in Table 2.

Table 2. Dependence of uncomplexed with PAA Zn²⁺ on concentration of K⁺ or Ca²⁺. Ph = 6.2, c(Zn²⁺) = 2.10⁻⁷ M.

c(K ⁺ or Ca ²⁺)	Zn ²⁺ - PAA + K ⁺		Zn ²⁺ - PAA + Ca ²⁺	
	log K	Zn ²⁺ %	log K	Zn ²⁺ %
0.004	6.5	0.03	4.4	3.4
0.01	5.9	0.21	3.7	16.0
0.03	5.1	0.73	2.8	60.8
0.1	4.3	4.1	1.9	92.6
0.3	3.6	19.9	1.0	99.0

As it is shown in the table, the fraction of the "free" Zn²⁺ increases with increasing of the concentration of K⁺ or Ca²⁺ ions. The influence of compete ion is much stronger using bivalent Ca²⁺ ions than in the case of monovalent K⁺ ions. For example, in the solution that contains 0.03 M K⁺, the fraction of uncomplexed metal was found to be 0.73 %. At the same time, in 0.03 M Ca²⁺ the fraction of "free" Zn²⁺ was 60.8%.

Processes described as the increase of the free metal concentration in consequence of acidification of the solution or of the growth of compete ions concentration may play an important role in natural systems, too. For example, the fraction of uncomplexed metal may change in case of acid rain or for example in conditions of mixing waters with low and high salinity in estuary.

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COMPARATIVE CHARACTERISTICS OF THE DISTRIBUTION OF HEAVY METALS, HYDRO- CARBONS AND ORGANIC COMPOUNDS IN THE PROCESS OF SEDIMENTATION AND PROGNOSIS OF THE EASTERN BALTIC DEVELOPMENT TILL 35TH CENTURY

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The question of geological evaluation of environment arises in the years of industrial development. Water bodies are most sensitive to pollution, therefore, their investigations are very important. On the other hand, it is a common case that all geoecological problems are related only to human activity. This leads to wrong environmental, economical and even political decisions and unnecessary waste of money.

A comparative analysis of summary and potentially polluted (ion, organomineral, hydroxide) forms of elements in the areas with different sedimentation, geographical, geological and climatic conditions makes it possible to determine the volume of pollution and reveal the predominance of natural or anthropogenic factors. What is the ratio between these two components in the investigated region since the pre-industrial period till active human activity nowadays and what are its future prognoses?

We present here the distribution of different element forms of C_{org} , $CaCO_3$, macro- and microelements (total number 18) and hydrocarbons in the thickness of sediments of Vistula and Kuršiu Marios lagoons, Finnish bay (Baltic Sea) and Hornsund fjord (Greenland Sea, Spitsbergen island) (Table 1 and 2). The considered thickness includes the period of the last 400 years of sedimentation. Quantities and ratios of element state forms are investigated in the layer which developed during the last 20 - 30 years and in the entire thickness. This allows to reveal

the ecological role of these forms in the cycling process of sedimentary matter.

Table 1. Comparative characteristics of total element contents in the sediments thickness of Kuršiu Marios lagoon, Finnish bay (E part), Vistula lagoon and Hornsund fjord (Spitsbergen).

Elements	Kuršiu	Finnish bay	Vistula	Hornsund	Relation a:b:c:d
	Marios (a)	(E part) (b)	lagoon (c)	fjord (d)	
	<u>0-10 cm</u> 0.115 cm	<u>0-3 cm</u> 0-10 cm	<u>0-5 cm</u> 0-65 cm	<u>0-5 cm</u> 0-284 cm	
C _{org} , %	<u>3.4</u>	<u>2.7</u>	<u>2.4</u>	n.i.	<u>1:0.8:0.7:-</u>
	3.7	2.3	2.3		1:0.6:0.6:-
CaCO ₃ , %	<u>19.3</u>	<u>5.9</u>	<u>10.8</u>	n.i.	<u>1:0.3:0.6:-</u>
	18.8	8.8	8.1		1:0.5:0.4:-
Fe, %	<u>1.3</u>	<u>5.8</u>	<u>2.5</u>	<u>4.2</u>	<u>1:4.4:1.9:3.2</u>
	1.8	5.0	2.8	4.1	1:2.8:1.5:2.3
Mn, %	<u>0.05</u>	<u>0.66</u>	<u>0.03</u>	<u>0.04</u>	<u>1:13.2:0.7:0.8</u>
	0.05	0.40	0.04	0.03	1:8.0:0.8:0.6
Cu, 10 ⁻⁴ %	<u>17</u>	<u>48</u>	<u>30</u>	<u>26</u>	<u>1:2.8:1.7:1.6</u>
	15	52	27	29	1:3.4:1.8:1.9
Zn, %	<u>52</u>	<u>195</u>	<u>107</u>	<u>92</u>	<u>1:3.8:2.1:1.8</u>
	46	176	115	91	1:3.8:2.5:2.0
Co, %	<u>12</u>	<u>49</u>	<u>20</u>	<u>42</u>	<u>1:4.1:1.7:4.5</u>
	12	78	22	41	1:6.5:1.8:3.4
Ni, %	<u>21</u>	<u>79</u>	<u>50</u>	<u>66</u>	<u>1:3.8:2.4:3.1</u>
	22	43	57	64	1:2.0:2.6:3.0
Cr, %	<u>43</u>	<u>136</u>	<u>66</u>	<u>93</u>	<u>1:3.2:1.5:2.2</u>
	43	139	67	99	1:3.2:1.6:2.3
Pb, %	<u>50^x</u>	n.i.	<u>12</u>	<u>68</u>	<u>1:-:0.2:1.4</u>
	46 ^{xx}		13	65	1:-:0.3:1.4

^x Layer 0-5 cm; ^{xx} Layer 0-24 cm

Table 2. Comparative characteristics of content of the element organo-mineral state form in the sediments thickness of Kuršiu Marios and Vistula lagoons and Finnish bay (E part).

Elements	Kuršiu Marios (a)		Finnish bay (b)		Vistula lagoon (c)		Relation a:b:c
	ppm	%from total	ppm	%from total	ppm	%from total	
Fe	<u>0.004</u>	<u>0.3</u>	<u>0.026</u>	<u>0.4</u>	<u>0.024</u>	<u>1.0</u>	<u>1:6.5:6.0</u>
	0.004	0.2	0.029	0.6	0.027	1.0	1:7.2:6.8
Mn	<u>0.004</u>	<u>8.6</u>	<u>0.030</u>	<u>4.5</u>	<u>0.013</u>	<u>38.0</u>	<u>1:7.5:3.2</u>
	0.005	10.0	0.030	7.5	0.016	38.0	1:6.0:3.2
Cu	<u>5.4</u>	<u>31.8</u>	<u>35</u>	<u>72.9</u>	<u>19</u>	<u>63.3</u>	<u>1:6.5:3.5</u>
	5.7	38.0	37	72.5	15	56.0	1:6.5:2.6
Zn	<u>9.1</u>	<u>17.5</u>	<u>21</u>	<u>10.8</u>	<u>34</u>	<u>31.5</u>	<u>1:2.3:3.7</u>
	5.2	11.3	29	16.5	30	26.0	1:5.6:5.8
Co	<u>1.3</u>	<u>10.8</u>	<u>4.0</u>	<u>8.2</u>	<u>9</u>	<u>45.0</u>	<u>1:3.1:6.9</u>
	0.4	3.3	2.5	3.2	11	50.0	1:6.2:27.5
Ni	<u>2.4</u>	<u>11.4</u>	<u>14</u>	<u>17.7</u>	<u>17</u>	<u>34.0</u>	<u>1:5.8:7.1</u>
	0.6	2.7	12	27.9	18	32.0	1:20.0:30
Cr	<u>1.9</u>	<u>4.4</u>	<u>26</u>	<u>19.1</u>	<u>12</u>	<u>18.2</u>	<u>1:13.7:6.3</u>
	0.5	1.2	20	14.3	13	19.0	1:40.0:26

The accumulation of heavy metals in the sediments of the Baltic Sea goes on a definite level of clark background [1]. In oxidation medium the clark concentrations of element diminish due to facial changes of sedimentation conditions and not due to diminishing of the role of reducing factor. High rates of sedimentation speed up to processes of reduction. The analysis of the change of lithogenic and hydrogenic forms of Mn, Zn, Pb, Cu, Ni, Co and Cd in the 30 cm thickness of bottom sediments in the Finnish bay revealed that even in the case of a 100 % dependence of hydrogenical forms on anthropogenic component it does not exceed 50 % from the total amount of an element in sediments [2]. This is in all cases below the clarks of elements in natural objects of lithosphere. In subsequent works it was shown that only in rare cases the average concentrations of hydrogenic forms exceed the content of lithogenic forms of elements [4]. This is especially

true of Pb, Zn, less - Ni, Co and Cu, i.e. elements which are more or less related to human activity and formation of compounds.

The interaction between the natural processes and compounds of industrial activity is most evident in the freshwater lagoons and bays of the Baltic Sea.

Diversity of the geological composition, different character and volume of nutrition with sedimentary matter, varying input of pollutants precondition dramatic changes of the distribution of biogens, macro- and microelements in all compared basins (Table 1).

The comparative data in Table 1 characterizes the chemical composition of bottom sediments in the zones of geochemical barriers which reflects sediment accumulation and present state of these three areas of active sedimentation. These data allow to draw the following conclusions:

1) Under the conditions of maximum contents of C_{org} and $CaCO_3$ in the sediments of Kuršiu Marios the content of elements is by 1.2 - 13.2 times lower than in the Finnish bay and by 1.5 - 2.6 times lower than in the Vistula lagoon. Similar tendencies while comparing with the sediments in the Hornsund fjord were also recorded previously [5-7];

2) The content of most elements (except Fe, Mn) decreases from bottom to top of the investigated thickness;

3) High concentrations of elements associated with terrigenous material reveal the prevalence of terrigenous process of sedimentation (under the conditions of relatively decreased amount of organic matter);

4) The decrease of the content of microelements reveal the predominance of natural factors in the process of sediment formation and an obviously secondary role of anthropogenic impact.

The scale of pollution of basins is revealed by investigations of elements' state forms. In the geological history of the sediment thickness they show the background state of sediments in pre-industrial times. Thus, the ratio of lithogemical and hydrogenical forms of Mn and Cr in the 14m-thickness of Holocene clays in the Gdansk bay has been actually stable during the whole period of its development [1]. Very often even background values of elements exceed their present levels in many sediment types of the upper sediment layer of Kuršiu Marios.

A comparative characteristics of organomineral (OM) form of elements, which is potentially most anthropogenic, in various sedimentation basins (Table 2) of the East Baltic show that absolute and relative contents of these elements are lower in the Kuršiu Marios lagoon than in

the Vistula and eastern part of Finnish bay (particularly). Depending on the genesis of sedimentary matter and geochemical dependence of elements the contents of OM form in the analyzed sediment thickness are by 3.1 - 40 times higher in the Finnish bay, 2.6 - 30 - Vistula lagoon than in the Kuršiu Marios lagoon. Therefore, the minimum pollution of sediments is evident. Its negligible volumes in the Baltic Proper are revealed in the work [4].

Sharp increase of concentrations in the Klaipeda strait, Nemunas and Neva mouths, undoubtedly, bear the tendency of human activity.

The presence of CHOP, PCB and HC, i.e. organic, most often human, products positively indicate pollution. A local pollution of the Klaipeda strait can be observed in stagnant-isolated areas of geochemical barriers. The improvement of their ecosystems require cardinal measures - deepening of the bottom, removal of wastes, construction of refinement equipment. Nevertheless, even in these cases the attention must be paid first of all to geochemical concentration of the material of exogenous processes in the course of technogenesis and not to the presence of toxic admixtures negatively effecting on the ecosystem.

A comparative characteristics of sedimentation which took place during the last few thousands of years in the Kuršiu Marios lagoon reveal the decrease of its rates from 5.7 (in the beginning) to 3.2 m/1000 yr (at present). The geochemical sedimentation evolution of the basin speeds up the natural processes of eutrophication, reduces the lagoon aquatory [6]. Neotectonic movements of earth crust lead to shore elevation in the NE Baltic and its relative subsidence in SW direction. For Kuršiu Marios this means up to 1.0 - 1.2 m/1000 yr. Under the impact of such subsidence and rapid sedimentation the direction of Nemunas course and its bed will change in the far future. Already in the 30th century Nemunas will carry its waters in SW direction. It will fall into Baltic Sea through the break in the basement of Kuršiu Nerija spit below Zelenogradsk. The Klaipeda port will gradually become an artificially deepened sea embayment. Lower rates of sedimentation in the Riga and Finnish bays [3, 4] but rapid elevation of the ground (up to 2-3 m and more in 1000 yr) will diminish these basins and, concomitantly, the Baltic Sea. A new geochemical situation will occur, scale of pollution increase and hydrological (consequently navigation) conditions change. The recent submarine Kolka shoal will develop into a spit, new sedimentation - ecological conditions in the Riga bay will occur. It will become more closed because Väinameri will become more

shallow and the acreage of Moonzund archipelago increase. The eastern shore of Finnish bay will become more shallow and shift closer to the continent, the Neva river regime will change. This far prognosis of the East Baltic has an ecological reflection in the present state of its development. In the course of gradual shallowing and freshening of the nearshore areas natural eutrophication increases as well as the volume of biogenic sedimentation. This alters understanding of geochemical environment, contents of elements, ratios of their migration and state forms. At the same time the image of basins pollution is strengthened due to insufficient elimination of organic compounds and pollutants from the natural process of sedimentation.

The presented material, preliminary given in work [7], demonstrates the necessity to create a new strategy of investigations of marine environment and new image about the environment pollution, change the existing MCL which do not correspond with the actual situation.

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USING OF MICROELECTRODES IN POTENTIAL STRIPPING ANALYSIS

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Microelectrodes are widely used as a conventional analysis techniques [1, 2]. The microelectrodes can be easily and cheaply assembled during analysis no stirring is needed in the analysis cell. However, while using classical potential stripping, the detection limits tend to be at least 10 times less than using glassy carbon solid electrode. One reason seems to be better access of oxydant to the electrode during the stripping phase, resulting in decreased stripping times.

In case of potential stripping analysis (PSA), stripping time is determinated solely by diffusion coefficients and concentrations of analyte and oxidizing agent present, and plating time, there is no current between the electrodes during stripping stage. Therefore, the electrode surface area doesn't have effect on analytical signal, and can write the equation for stripping time t_s :

$$t_s = (D_{\text{red}} [\text{Red}] t_p n_{\text{red}}) / (D_{\text{ox}} [\text{Ox}] n_{\text{ox}}) \quad (1)$$

where t_p - plating time;

[Red] - concentration of analyte in solution;

[Ox] - concentration of oxidizing agent in solution; respectively;

n_{red} , n_{ox} - amount of electrons transferred in electrochemical reaction.

The diameter of the fibre electrode is less than the minimum diffusion layer thickness, therefore, mass transfer rate isn't influenced by stirring, at least, partially.

Microscopic working electrodes were used in the Tartu Public Health Service for analysis of heavy metals (Pb, Cd, Cu, Zn) by PSA. Properties of carbon and gold fibre electrodes have been investigated.

A set of instruments including potentiostate PA3, recorder XY-4103 (both Laboratory Pristroje, Prague), high-impedance electrometer (University of Tartu), electrode cell TTA-80 (Radiometer, Copen-

hagen) and a commutating block, was used for PSA measurements. Saturated calomel electrode K-4040 was used as a reference electrode, platinum electrode P-1312 was used as an auxiliary one (both Radiometer, Copenhagen). As working electrodes, self-made carbon fibre microelectrodes or gold fibre microelectrodes were used.

For preparation of the microelectrodes, 0,2 mm copper wire was joined with carbon fibre (7 μm , Goodfellow, Great Britain) or gold fibre (25 μm , Goodfellow) using a conductive silver containing spray (Electrocure, Kent, Great Britain). The spray was allowed to harden for 20 minutes, and a second layer was applied; after that the electrode was left to stay for 5 hours.

Electrodes were sealed in pipette tips (Finntip) using epoxy resin (EPO, Estonia). As alternative methods, heating and polyvinyl acetate glue (PVA, Estonia) were used. Unfortunately, the conductive spray used, didn't stand heating, therefore, contact between the copper wire and the fibre was broken. It was easy to seal the electrodes with polyvinyl acetate glue, but the copper wire used dissolved in the glue, giving a visible green dye and, apparently, a high copper leaking into analysis cell.

Tridistilled water was used for preparation of solutions. For preparing a supporting electrolyte, 10 M molecular distilled hydrochloric acid was used. Working solutions for lead and cadmium were prepared just before measurements by diluting $5 \cdot 10^{-5}$ M solutions of lead(II) and cadmium nitrate; for copper $4.80 \cdot 10^{-5}$ M solution of CuSO_4 , and for zinc $6.15 \cdot 10^{-5}$ M solution of $\text{Zn}(\text{NO}_3)_2$, were used for additions. For amalgamating the electrodes, mercury(II)nitrate solution containing 1 g/l Hg^{2+} , was used.

Gold electrodes were rinsed in concentrated nitric acid solution to obtain a clean solution. Various lengths of gold electrodes were used, from 1 mm to 20 mm.

The microelectrodes were amalgamated using $\text{Hg}(\text{NO}_3)_2$ solution containing 0.05 g Hg^{2+} /l, 4 plating/stripping cycles were performed at potential -0.95 V. After that, electrodes were rinsed with tridistilled water and immediately placed to analytical solution. Analytical signals of lead, cadmium, copper and zinc were recorded at various concentrations. Plating potentials for lead and cadmium were -1.1 V, for copper -0.95 V and for zinc, -1.3 V. Detection limits of $5 \cdot 10^{-8}$ M for Pb^{2+} and Cd^{2+} at plating time of 4 minutes were achieved, for Cu the detection limit was 10^{-7} M, and for Zn the limit was 10^{-6} M.

Low sensitivity of zinc determinations can be explained by enhanced hydrogen forming on electrode surface at higher potentials. For zinc determination in food samples, however, the sensitivity is sufficient in most cases, as zinc occurs there at levels of several ppm.

Two ways to increase the sensitivity can be considered for stripping chronopotentiometry. Removal of air from the analytical solution is widely used, but the technique significantly increases analysis time. The other way is to use stripping at controlled current, in this case more complicated instruments are needed for analysis.

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SAMPLING AND ANALYSIS OF ORGANIC DUST AND SOME OF IT'S COMPONENTS

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Information about exposure-response relationships is essential for the setting of permissible levels of occupational exposure. These relationships have proved to be difficult to verify for organic and vegetable dusts of agricultural origin. The concept of vegetable dust is quite broad including grain, tea, coffee, tobacco, sisal, flax, hemp, cotton, mouldy hay and sugar cane. The common denominator of these dusts is the disease they cause in workers. Here we shall restrict our review to cotton, which is a very important occupational problem in industrial countries.

It has been evident since the first incidences of byssinosis in cotton textile mills that this disease is caused by foreign matter rather than by cotton.

The complex composite "cotton dust" is defined as dust generated into atmosphere as a result of the processing of cotton fibres, combined with any naturally-occurring materials, such as stems, leaves, bract, micro-organisms and inorganic matter which may have accumulated on the cotton fibres during growing and harvesting.

By 1942 it was suggested that acute illnesses among rural mattress makers using low-grade cotton was caused by the inhalation of gram-negative bacteria. Between 1942 and 1944 there were reports on the total bacterial and aerobacter cloacae populations in cotton bales from different growing regions in the U.S.A, and the presence of endotoxins in cotton dust was demonstrated. The bacterial contamination of cotton dust was further by Rylander and Lundholm in 1978, and in 1979 Rylander et al. demonstrated a correlation between gram-negative bacteria in cotton and acute airway constriction [1]. Apart from endo-

toxins, other causes have been suggested, such as histamine, histamine-releasing pharmacological agents and proteolytic enzymes [2-7].

In cotton mills complex symptoms other than byssinosis are also known as "mill fever". The relationship between mill fever and the Monday morning sickness associated with byssinosis is still unknown, but the causative agents may be micro-organisms in excessive concentrations. There is insufficient data for a proper prevention programme and it is important that the etiological agents be identified and that the significance of airborne micro-organism fungus spores, gram-negative bacteria and their endotoxin and histamine-releasing pharmacological agents be measured.

Gravimetric determination of cotton dust

There has been little standardization in the methods used to measure the dust levels in mills. All the national and international recommendations for the maximum permissible exposure levels of cotton dust suggest that gravimetric determination of dust be used to monitor working conditions.

From the occupational hygiene point of view, the dust levels measured in cotton manufacturing areas can be influenced by such factors as the type of samples, the type and grade of cotton being processed, and the type of operation being carried out on the cotton. As cotton moves down the production line to become a finished product, each processing operation removes undesirable trash and short fibres from the cotton [8]. It is normal practice to consider the dust levels for the various processing operations separately.

Total dust concentration is a common but crude measure of exposure level, because the identity of the agents responsible for the various effects is not known, and the major part of sampled dust consists of lint.

Apart from total dust sampling, samplers which measure only the smaller dust particles have also been used [9].

Considerations of the complexity of cotton dust led to the recommendation that a vertical elutriator with a nominal 50 % cut-off-size at 15 / μ m as the first stage of a standard sampler-vertical elutriator has to be used. The second stage is analysed to ascertain the mass concentrations of the particles judged most likely to be related to health effects [10].

Weighing errors caused by adsorbed water are reduced if the pre- and post-experimental sample weighings are made when the water content of the air in the weighing environment is the same. The use of the reference filters should also be considered to check weight differences. It is also recommended that less hygroscopic filter materials, such as PVC or teflon, has to be used to reduce the amount of adsorbed water affecting the weighting. The latest solution to the adsorption problem is the use of matched-weight filter pairs. These are pre-weighed by the manufacturer to within a 0.1 mg tolerance. The filter pair is fitted into the same filter holder, and the top filter collects airborne particles, while the bottom filter acts only as a control. There is thus no pre-weighting of filters in the laboratory, which makes the work faster and simpler.

In many published studies a relatively close relationship has been found between elutriated dust levels and the prevalence of byssinosis. Also variations have been found in the prevalence in different mills, although their dust levels are similar. This indicates that there are still factors which are not described by the gravimetric measurement of the dust at cotton-processing sites.

Pharmacological agents in dust

The results of many studies indicate that plant waste components, including leaves and bract, may contain varying amounts of potential byssinosis causative agents. These agents are natural toxic constituents of the plant tissue, such as, terpenoid aldehydes and polyphenols [5, 7, 11]. The characterization of the pharmacological agents is made difficult by the diverse nature of the trash in raw cotton which forms the major part of the respirable dust in mills. There are botanical differences between the trash in different parts of the world. Many of the published papers on plant waste are from U.S.A. where harvesting has been mechanized since 1940's. In East Africa cotton is only picked manually, which means that bracts are a more important components of the trash than the leaves.

The direct analysis of pharmacological agents is not sufficiently developed for routine assay methods to be used and there are still too many contradictory suggestions for the causative agents to permit the adoption of universal control measures [6, 12, 13].

Collection and analysis of airborne micro-organisms

Micro-organisms can be collected either by area sampling, using stationary monitoring or by individual sampling. The correlation of health effects with concentration levels is best performed by sampling individuals close to the breathing area.

Several collection devices are available and these may be divided into the following categories:

- a) impact in liquids, impinger samplers [14];
- b) impact on semisolid surfaces, cascade impactors [15];
- c) filtration, gelatin or membrane filters [16];
- d) settle plates, Petri dish [17].

Filtration and impact in liquids has some advantages over the more commonly used impact on semisolid surfaces (Andersen sampler) or settle plates. These methods have their limitations and industrial hygiene practitioners should be aware that, although a quantitative count is generated, the number represents a relative quantity dependent upon media selection, incubation temperature, the viability of the organisms, separation of fast growing species from slower-growing species, staining technique, season and time of day sampled, etc. The variations are numerous, and the results must be interpreted carefully.

Because it is suggested that bacterial endotoxins play important role in causing diseases in dusty work places there are analytical interests to define this compound directly without long incubation period to determine species of airborne microorganisms.

Besides bacterial impurities organic dust contains also moulds with toxic spores. The basic task in microbiological laboratory besides the determination of species is to test mycotoxins.

Microorganisms synthesize many organic compounds, which can be analyzed with modern techniques such as gas chromatography and mass spectrometry. Some of these, like muramic acid, can be a microbial chemical markers for endotoxins in Gram-negative bacteria because it is prominent [18].

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METHODS OF MONITORING WORK ENVIRONMENT

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There are number of different methods that can be used to recognize occupational hazards. A typical occupational hygiene evaluation of a facility includes both a visual inspection and workplace measurement. To ensure a safe work environment in production plant, hospital operation room, laboratory or just in an office, it is usually necessary to monitor quantities of organic vapours, inorganic gases and aerosols in air. Basically occupational hygiene monitoring involves sampling and analysis. Both of these processes go hand in hand and are dependent on each other for evaluation of personal exposure and assess health risk. It is beyond the scope of this presentation to discuss the entire subject of occupational hygiene and the emphasis has been placed on the basis techniques: sampling, recovery, analysis by various techniques and computers.

In the past ten years the occupational hygiene monitoring has expanded from industrial environment to both community and global environments. This has led to improvement of analytical techniques and methods for detecting trace airborne contaminants and emissions. Specially rapid development has been for indoor air and building material emissions. This has been very challenging because of the multitude of materials and the complex matrix of contaminants. The concentration range has lowered sometimes down to part-per-trillion range. The emphasis has been given to organic materials such as aldehydes, halogenated hydrocarbons and polynuclear aromatics.

There has been a great improvement in analytical instruments in the laboratory and for field applications partly because of taking in use computers and plant wide networks to obtain and analyse data. Those

equipment allow to establish databases and data can be utilized more completely than earlier by occupational hygienist.

Sampling on sorbents and filters

Solid sorbents are used extensively to sample contaminants in air. A number of different sorbent media have been utilized for collecting various gases and vapours. Charcoal is the most popular choice for organic vapours, while silica gel is used for polar organic vapours. Tenax and XAD resins have proved to be useful for specific purposes.

Solid sorbents are convenient to use and can concentrate vapours. Liquid containing impinger bottles have been used to collect airborne contaminants such as gases, mists and aerosols. Beside impinger bottles for some gases there are also inert plastic passive liquid dosimeters available on markets. These can be sealed after sampling and sent to a laboratory for subsequent analyses.

There are two basic techniques for collection substances. The most popular utilizes a small battery operated pump to draw the air through the solid sorbent. The second technique utilizes diffusion of compounds into a badge containing solid sorbent. All of these sorbents can be used for both active and passive sampling and for personal and area monitoring.

In most cases the compounds are recovered from the sorbent by solvent elution, e.g. carbon disulfide. Thermal desorption is coming more and more popular because the preparation of samples can be mechanized and combine with computers to automated analysis system on the presumption that analytes are not labile and there is no need for subsequent analysis.

Improvements in sorption techniques have been made by impregnating some sorbents with reagents capable of reacting with and stabilising such as amines, isocyanates and aldehydes.

There are many ways preconcentrate the sample to improve analytical sensitivity and eliminate matrix interferences.

The particulate collector may consist of one or a combination of devices such as a filter, sorbent tube, impinger, cyclone and impactor. There are several specific filter media to be used. Polyvinyl chloride (PVC) filters are used for gravimetric determination of total dust. Cellulosa esters can be dissolved in acids and are preferable to be used for metals.

Fibers as asbestos are still collected on membrane filters in nonconductive cassettes. These filters are cleared and mounted on a microscope slide for counting by phase-contrast light microscopy. Qualitative bulk fiber identification is done by polarized light microscopy. For confirmatory analysis transmission or scanning electron microscopy is used.

Proper evaluation of worker's exposures necessitates taking valid quantitative exposure measurements, interpreting these measurements and exercising professional judgement.

One important side of modern occupational hygiene is to harmonize sampling strategy. Many recommendations are available like CEN (Comite Europeen de Normalisation) Working group 1 have been presented a draft proposal for measurement strategy in occupational hygiene.

Conventional sampling with pumps and sampling media can be used to verify the compliance of the exposure but does not provide very good insights to the reasons for the excessive exposure. To overcome this problem the video exposure monitoring technique was developed to characterize workplace exposure as a function of time.

Recovery

Preparation of gas and vapour standards or the generation of dynamic atmospheres with known concentration is an important aspect of air analysis and monitoring. Calibration of air analysis, including sources of error like poor recovery, evaluation and minimization of uncertainty, linear relationships and intercalibration are usually carried out in a dilution chamber. Preparing parts per billion (ppb) levels of volatile organics is a challenge due to background levels, detection limit of instruments, adsorption on container walls and preparation of primary standards. New inventions and materials allow to build calibration systems for the demands of the times.

Improvements have been made also in recoveries of mixtures of polar and nonpolar agents. By investigating desorption solvents it has been found that addition of suitable compounds to carbon disulphide, e.g. 5 % formic acid or 2-butoxyethanol, may improve recovery of oxygenated contaminants.

Selection of filters can be a critical factor in determining recovery rates of some reactive aerosols like isocyanates or inorganic compounds.

In chromium containing aerosols recovery rates from Teflon membrane filters were higher than those from glass fiber or PVC filters.

Analysis

References to the analysis of specific chemicals over the few past years are thousands and too numerous for brief marks. There are some exceptional good books published like *Metals and their Compounds in the Environment* or review articles like one of the environmental and occupational importance of polynuclear aromatic hydrocarbon (PAH).

Chromatographic analyses continue to be the most versatile and widely used analytical techniques. As more complex mixtures are determined in the work environment, there will be a continuing emphasis on employing capillary gas chromatography. As mixtures comes more diverse, the use of GC/MS and multidimensional chromatography becomes more and more important. With these moderns instruments one can maintain better resolution of peaks and shorten the analysis time needed for unknown mixtures.

Automation continues to play an important role in occupational hygiene laboratories and field work. This has applications in sample preparation work. More robotic systems are taken in use every year applied for thermal desorption organic pollutants or analysis of lead in blood by atom absorption spectrophotometer (AA).

Computers

Few invention has revolutionized the occupational hygienst's job as much as the microprocessor. It has been incorporated into nearly all laboratory equipment and instrumentation and the benefits have been widely accepted. The requirements for automation are that the instrument must be left to run automatically without operator attention. In all kinds of instruments simple electronic integrators have been replaced by powerful microprocessor based datahandling system, which could simultaneously receive data from more than one source and could control the chromatographs linked into the analytical system. Automatic sampling and injection devices changed from being simple mechanical machines which receive instructions from timers to sophisticated robots. the first working system in 70's were expansive centralized computers and programmes were tailored for specific needs of the client.

Introduction of personal computers (PC's) provided an attractive lower-cost alternative to centralised computer system. Until middle 80's PC's were not seriously considered for chromatography automation with their relatively slow processing speed, low-resolution monitors and limited memory capacities. After developed PC hardware to meet the needs it took some time when software packages were available. In the beginning they were menu driven and highly text oriented and very difficult for first-time casual user to operate. Two developments in the middle of 80's changed the situation. The first was popularization graphic oriented software by Apple Computer. The second achievement was introduction of MS-DOS Windows by Microsoft Corporation. These revolutionized the way in which the user interacts with his or her computer.

After that phase the laboratory information and managements systems have entered the information age. Hardware prices have decreased to the point where even a small laboratory can afford a PC. Excellent standard applications are available for integrating small complex peak groups in chromatography, store data, prepare reports, compare results with standards. By following few simple rules, any laboratory can benefit from better management and quality assurance programmes. PC's allow more versatile use applications of statistical and mathematical methods in occupational hygiene. Computers bring with themselves many problems to manage, increase and availability staff training resources, computer security should be evaluated, planning is difficult in the long run due to rapid and unpredictable advances in computer technology.

There seem to be many software applications available for those activities which we share with more populated field like office routines, management of laboratories, measurement control and CD-ROM data bases. Pure occupational hygiene and safety fields have only few prepackaged computer solutions. Computers are technological advances and technology is manageable if the applications are not available we can make them.

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TRAPPING AND ANALYSIS OF ORGANIC INDOOR AIR POLLUTANTS

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To monitor and control the general environment, it is important to know the concentrations of chemical pollutants in the air. Indoor air presents a special analytical challenge, the variety of possible compounds that can be found in the indoor is enormous. The common method to trap, concentrate and analyse pollutants includes sample tubes containing solid sorbents which adsorb certain gases and vapours for subsequent gas or liquid chromatographic analysis. A calibrated pump draws air through the tube so that the average concentration over the period of sampling is the quantity of material collected divided by the volume of air sample.

Many sorbents have been proposed for indoor application of environmental analysis. Some sorbents are coated with reagents which form stable, specific and analysable derivatives. This is the most effective method of collection, but such methods based on chemical adsorption are mostly specific to a single chemical or group of chemicals. Porous materials that collect molecules by physical adsorption are very popular, since a wide variety of compounds may be collected on a single sorbent. Collection efficiencies vary widely from analyse to analyse. Sorbents commonly used include charcoal, silica gel, alumina, molecular sieves and porous polymers. The choice of trapping sorbent and the method of desorption can significantly influence the compounds that are detected. The two major desorption methods are liquid desorption and thermal desorption. The adsorbent Tenax (Supelco) is a good sorbent for thermal desorption and analysis of non-polar, midrange boiling compounds, and the thermal desorption temperature can be up to 300 °C. Charcoal is a good and commonly used

sorption material for all kind of non-polar analytes and moderately good for most interesting polar analytes. Adsorption capacity of charcoal is several magnitudes higher than of Tenax TA. Charcoal needs liquid desorption which is easier to manipulate but has in many cases poorer detection limits because of small aliquot utilized in analysis.

In this study two adsorbents, charcoal and porous polymer Tenax TA were used to sample polar and non-polar organic compounds at low concentrations in indoor environment. The main emphases was paid on differences in results from these two trapping materials.

Experimental

Samples were collected from an indoor environment with air quality complains with SKC-222 portable vacuum pumps at air flows from 50 to 70 ml/min. Thermal desorption was conducted by using ATD-400 thermal desorber (Perkin-Elmer, UK), which was directly interfaced with GC. The applied desorption temperature was 250 °C. As gas chromatography HP 5890A (Hewlett-Packard, USA) with Ultra 1 capillary column was used. The qualitative and quantitative measurements were made by HP 5971A mass specific detector with scan 10 - 650 ma coupled to computer with HP G1030A integration program and Wiley data base of mass spectra. The application for thermal desorption and gas chromatography is published by Perkin-Elmer (Perkin-Elmer Ltd., UK) and in series of validated methods by UK Health & Safety Executive [1]. Liquid desorption was conducted by extracting the charcoal tube samples in carbon disulphide according to Finnish standard SFS 3861 (Measurement of organic vapours in workplace air with charcoal tube method) [2]. The charcoal tube standards were prepared according to phase equilibrium method [3].

Results

In Table 1, the results of collection of four parallel samples of indoor air at five locations, two samples collected on Tenax TA and two collected on charcoal, are presented. Different chromatographic patterns are evident. If only one of the adsorbents is used in the analysis, the interpretation of the airborne organic load at the location can be quite different.

Table 1. Comparison of concentration of volatile organic compounds in sample pairs collected on Tenax TA with thermal desorption prehandling versus collection on charcoal tube with liquid desorption.

n-Butanol (mg/m ³)		Hexanal (mg/m ³)		Toluene (mg/m ³)	
Tenax	charcoal	Tenax	charcoal	Tenax	charcoal
24	156	187	158	22	26
31	155	138	151	39	26
97	234	160	9	31	37
89	211	131	8	38	34
76	205	244	36	37	32
78	204	173	45	39	33
35	68	30	3	50	44
30	72	22	4	38	44
42	75	45	12	22	25
45	66	41	10	21	20

Discussion

Sampling on solid sorbent material is the most common method used in indoor air analysis. Sorbent trapping has the major advantages of low cost and transportability. A portable pump is used to draw a volume of air through a sampling cartridge loaded with the sorbent. After sampling the sorbent tube loaded with organic pollutants is returned to laboratory and desorbed using either solvents or heat and analysed with chromatography.

Due to great discrepancies among these results of two common sorbents there is need to evaluate both the sampling situation and analytical procedures. The most useful measure of the performance of a solid sorbent tube is the safe sample volume (V) without breakthrough. The safe sample volume can be estimated from breakthrough volumes (BTV), which can be determined experimentally. The safe sampling volume of buthanol on 200 mg Tenax is 5 liters air as given by MDSH 72 [2], which means that during long sampling period the weaker sorbent will leak. On the other hand the strong adsorption on charcoal is disadvantageous when monitoring hexanal. It is seen in Table 1 that calculated hexanal concentrations are lower. The desorption efficiency is

poor from charcoal when extracting with carbon disulphide. The third component toluene seems to behave as expected and results between Tenax and charcoal are near each other.

The adsorption-desorption system of multicomponent samples seems to be very difficult to control for various environmental sampling requirements and it has several limitations, i.e. break through and desorption efficiency which should be covered before interpreting results.

The possible solutions for keeping some level of comparability between environmental monitoring methods in official use, including trapping and analysis, is to refer to the well established standard method.

In an effort to overcome the bias that results from the use single adsorbent, research workers are using tubes with multiple sorbents packed in layers. The use of multisorbent can greatly extend the applications of trapping organic pollutants on sorbents.

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VOLTAMMETER ANALYSIS (TUNNELING SPECTROSCOPY OF ELECTRONIC POLARIZATION)

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At present tunneling spectroscopy has received the wide distribution the main feature of which is the electron loss of energy $h\nu$ on molecules in barrier when an electron is tunneled through a barrier. The loss of energy is connected with the availability of exiter molecules in the form of electronic transitions and oscillatory changes of adsorption state in the barrier of molecules.

Such a inelastic process provides the additional channel for occurrence of current, as a result which on voltammeter curve the bend at some threshold voltage φ_0 such that $e\varphi_0 = h\nu$ (where $h\nu$ - energy of excitation centre of adsorption is found out, and φ_0 - presents the potential of emitter).

Since there is a large quantity of such frequencies, stimulate significant number of breaks on the voltammetric curve and can speak about spectrum studied molecules. It is to be expected, that this spectrum is connected with absorption spectrum of given substance in infra-red, visible or ultra-violet areas [1].

Usually in tunneling spectroscopy a low pressure is used and the energy of which is comparable with the energy of infra-red radiation. Therefore, so far, as a rule, the oscillatory characteristics of adsorbed particles [2] were investigated. The processes of tunneling are sufficiently theoretically justified to permit to describe the interaction of electrons of metal with molecules of adsorbates, to define (determine) their natures and orientation on the surface, to reveal their various transitions, concentration adsorbed of substance, etc., which are inaccessible when considered from the viewpoint of classical interfaces [3].

In the electrochemical experiment during cathodic polarisation, generation of electron occurs [4], which can be described by the same expressions as tunneling spectroscopy. Here is also analysed voltammetric curves and the change of conductivity on alternating current in kind of $C-\varphi$ or dependences (C - the differential capacity of double electrical layer).

Classical polarographic curve of restoration of ions of cadmium from water solution on Hg represents the process of interaction of electrons from metal with ions of cadmium on the interface, which is realised at potential -0.63 V (against N.C.E.). At this potential the maximum [5] appears on the $C-\varphi$ curve. The addition of adsorbate capacity (in [5] - $(C_2H_5)_3PO_4$) causes the change in both voltammetric and capacity curves. On voltammetric curve the new half-wave, on capacity curve - new maximum occurs at potential appropriate of restoration $(C_2H_5)_3PO_4$ and the size of current of restoration of ions cadmium and the height of maximum on the $C-\varphi$ curve are reduced. At a enough high concentration of $(C_2H_5)_3PO_4$ the maximum on $C-\varphi$ curve appears as break on $I - \varphi_1$, because of total filling of surface Hg by molecules of adsorbate.

Since the polarographic half-wave potential $E_{1/2}$ is connected with potential of maximum on voltammetric curve in this work an attempt was made to establish a correlation between potentials of half-wave potentials of polarographic spectrum and energy $h\nu$ of the process of excitation electron of various substances. For 23 substances (for which data of half-waves potentials and of optical spectra are available) the correlation is submitted in kind of linear dependence in coordinates $E_{1/2}$ (in absolute scale of potentials [6]) - $h\nu$ with tangent of inclination equal to 1. This means, that the maximum optical absorber and the break on voltammeter curve has equal energy.

The research of capacity characteristics at metal/solution interface in presence of various organic substances has revealed the main feature of the $C-\varphi$ curve; their independence from the nature of the metal and its phase conduction. Thus many systems quantitatively concurrences of height, forms of maxima and potential (measured concerning to the same reference electrode), so named adsorption-desorption peaks (the Figures 6-5 in [7] are observed not only qualitative.

The comparison of potentials of adsorption-desorption peaks for different metals shows, that their position practically coincide. Thus the average significance of absolute potential of adsorption-desorption peaks

$n\text{-C}_5\text{H}_{11}\text{OH}$ on added in [7] metals makes approximately -3.3V and, obviously, corresponds simple affliating electron emission from metal to molecule of adsorbate [8] with formation anion-radical. (Unfortunately, it was impossible locate in to relevant literature the optical spectrum of associating the appropriate process of electron to spirito).

Therefore we are deprived the opportunity to consider the peaks to be coupled with adsorption-desorption relating to this process in [9]. That the areas of frequencies, appropriate $3.13 - 3.3 \text{ eV}$ the band radiation of $\text{C}_2\text{H}_5\text{OH}$ is observed, but whether it is by reflection just this reaction requires further research.

In absence of specific adsorption for such metals as Hg and Bi on $\text{C-}\varphi$ curves a wide peak occures at anodic potentials [10-12]. Just in this area of optical spectrum the band of adsorption of light OH^* [13] begins. At availability in presence of specific adsorption in anodic area also the peaks of capacitance exists, mirror-symmetric to maxima of cathode [7], but greater intensity occur. A similar phenomena may be observed in optical spectra of absorption and fluorescence [9, 14].

Thus in analytical practice the application of methods of simultaneous research $\text{I-}\varphi$ and $\text{C-}\varphi$ dependences permits to unite polarographic analysis with optical spectra and enables considerably deeper understanding of the processes and phenomena occurring in nature.

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ATTACK BY ENVIRONMENTAL OBJECT AND VOLTAMMETRIC CONTROL

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The problem of the environment protect as a rule we bind up with life and health of people, animals, fishes and birds, with the protect of plants, soil and natural water. But the environment is known to cause corrosion in electronic devices, constructions and structures under service conditions their reliability, service life parameters deteriorating to some extent. In principle, these attacks may be produced by nature itself. In the first place there are the air and the water. The natural air attacks are aggravated in cases where the former is damp and still more where it is saturated with seawater fumes. The same holds true for the water. Its corroding attacks become stronger in the case with sea water.

Under the existing conditions, the environment attacks causing corrosion are aggravated by man's economic activity. This activity is leading to dramatic changes in the air and water composition, in particular, in the regions of industrial cities and in production areas, in rural districts with intensive use of fertilizers and pesticides. Gas and aerosol attack of industrial wastes are especially widespread and are able to take effect in the following way: to cause corrosion; to produce corrosion active substances while dissolving in water fumes; to produce the medium provoking corrosion separately or in combination with some other substances.

The industrial waste composition is variable. It depends on many factors, such as the kind of products yielded, technology improvements, availability of cleansing systems.

The air layer at the Earth's surface reaching to a height of 10 - 12 km is a gaseous mixture with more or less steady composition. The basic components of the mixture are nitrogen, oxygen, argon and carbon dioxide. Besides gases, the atmosphere air always contains a certain

amount of various admixtures, with result from chemical and physical conversion in nature and man's economic activity. The latter has a strong impact on the city air, the air composition in vicinity of industrial enterprises, rural districts and woodlands, subjected to chemical treatment with fertilizers, pesticides and herbicides. Therefore it is customary to speak about the harmful influence of these factors on man, the fauna and flora. All this is true, but it is expedient to consider the present day atmospheric air as the medium stimulating corrosion processes. The time is likely to come when the working out of not only the maximum allowable concentrations for substances harmful for health but for proper performance of radioelectronic devices, constructions and structures for the expected service time, will be necessary.

All this means that at present there exists a pressing necessity to set control of the atmospheric air. One of the possible methods of control is voltammetry. This technique is rather universal. It displays high sensitivity to determine from one to five substances simultaneously. Voltammetry is a high-sensitivity technique for identifying the micro-content of various substances of both organic and inorganic nature. This accounts for its applications, control over environmental objects such as the atmospheric air, reservoir water, underground- and wast-water, occupying an important position among them.

For a long time the air has been a traditional subject for voltammetry. The technique is used in analysing the atmospheric air, the air of production areas and the air in the vicinity of industrial enterprises. Thus, organic and inorganic gases, aerosols, liquid fumes and dust are determined by the voltammetric technique. There are comparatively few polarographic technique for analysing the atmospheric air. But recently a great number of technique dealing with analysis of different substances in the air of production areas have been proposed. These techniques are fully applicable for analysis of the atmospheric air. However, it is necessary to take into account the fact that the concentration of substances under investigation is far less then that of the other.

For many substances the content in atmosphere do not exceed hundredth, thousandth and ten thousandth fraction of mg/m^3 . Hence highly sensitive methods are used for their analysis. The development of voltammetry technique is favoured by following. The technique is considerably universal and while analyzing objects have gaseous, liquid or solid state, both organic and inorganic substances are possible to be determined. The technique is of high sensitivity. It allows to indicate

micro- and ultramicro concentrations of substances. Thus, at the analysis of the atmospheric air the lower limit of detection determined amounts 1 - 0.0005 mg/m³, 1 - 0.01 mg/l for water and 10⁻⁵ - 10⁻⁷ % for solid. The technique is of high precision, which is typical for all electrochemical methods, voltammetry among them. The voltammetry technique allows to identify the valence of substances, for example to determine separately 6 and 3 valence chromium. Voltammetry it possible to determine up to 5 elements simultaneously. The asset of technique is a low cost of an analysis instrumentation and chemical agents.

Polarography and voltammetry are possible to use for determination for example:

- non-metal: sulphurdioxide, ozone, nitrogenoxides, sulphur, sulphate-ion, sulphite-ion, chlorine, fluorine, hydrogen chloride, cyanogen, hydrocyanic;
- aerosols of metals, semi-conductors and its combinations: barium, iron, cadmium, lithium, manganese, cupper, tin, lead, selenium, selenic anhydride, thallium, tellurium, titanium, chromium, chrom-oxid, zinc, molybdenum, nickel, cobalt and other;
- organic substances penetrating into the atmosphere and water as a result of the ejection by industry producing organic materials and and also as a result of using fertilizers, pesticides, insecticides and herbicides.

Thus, the voltammetry gives us a chance to use it in an environmental control. It is necessary, because the environmental objects contain many substances harmful for man and for the objects around them.

AUTOMATIZATION OF VOLTAMMETRIC APPARATUSES

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Voltammetry is a high-sensitivity technique for identifying the micro-content of various substances of both organic and inorganic nature. This accounts for its applications, control over environmental objects, such as the atmospheric air, reservoir water, underground and wastewaters, occupying an important position among them. The voltammetry analysis time includes:

1. *Sampling time*. Depending on the object tested, this time may constitute a few tens of minutes to 24 hours and more. The substances of the objects being not complexed, readily to be analyzed are sea water, reservoir water, industrial flushing and recycling water, electrolytes in plating and pickling baths, drinking water, specially purified water, fast soluble agents and aerosols in atmospheric air. In case of analyzing hard-soluble substances, either a simultaneous sampling of several specimens (10 - 40) or sometimes methods of partial extraction of the substance determined for the purpose of control efficiency increase are used. While analyzing complex substances, the efficiency increase is due to the application of voltammetry modes distinguished by their high resolution, as well as to a more simple sampling without separating the base and interfering components. Under technological laboratory conditions it is generally a manual operation using some automatic devices for certain aims. For sampling standard uniform specimens, there are automatic devices involving weighing out samples, conveying reagents, mixing, heating and cooling by the present program.

2. *The analysis time* does also involve the time for setting a voltammetry mode. The distribution of the time might be rather intricate. Thus, with the indicator being a mercury film microelectrode,

the time is to be set for electrochemical cleaning the electrode at the positive potential; upsetting the mercury film at the zero potential, blowing through the solution to remove the oxygen from it, accumulating the substance at the designed potential with an intensive mixing of the solution; setting down and recording the voltammogram. For the purpose of obtaining averaged results the aforementioned operations are repeated 2 to 5 or more times. At the analysis of a sole sample, this time runs about 20 minutes to 1 hour and more. The duration of this stage might be slightly decreased only at the expense of applying fast sweep potential modes. However, the advance of a programmed automatic control over the instrument enables the operator to be relieved of hard monotonous as well to improve precision and reproduction of the data obtained. This mode is particularly advantageous at the analysis of uniform samples for one and the same set of components determined

3. *The data processing time* involving the calculation of the concentration or the content of the substance determined in the sample on a calibration chart with the method of a standard solution addition or the method of standard solution, the determination of the standard deviation and confidence coefficient. While calculating the behaviour of the voltammogram for the supporting electrolyte throughout the sampling procedure is taken into account. The time is appreciably dependent on the automatization of the data processing and the calculation. In the absence of automatic data processing means this stage takes one hour or more. With complete automation this time is within 1 minute.

The state-of-the art development of microelectronics and computing technique makes allowance for widening abilities of voltammetric instruments both in terms of a considerable improvement of analytical characteristics (sensitivity and resolution) and increasing the efficiency by means of automating a laboratory analysis. These two aspects should be elaborated simultaneously. The analysis of the state-of-the art voltammetry shows those trends to be advantageous, ably to cope with the above problems. That's why the variant of an instrument approach should be regarded from the viewpoints of both attaining extreme parameters in determination and possibility of automating an analytical process, which permits to solve the following tasks:

- to carry out automatically repeated records of voltammograms, averaging characteristics and recording an averaged voltammogram;

- to exclude from the number of the averaged signals the values different from the average signal by an order of magnitude greater than the present error of the experiment;
- to determine the concentration of the substance and calculate electrochemical constants;
- to calculate the standard deviation and the confidence level of the experimental data;
- to represent experimental conditions and results in quantities of current or concentration with the reference quantities being pre-assigned;
- to derive the difference voltammogram, where the subtracted signal is a supporting electrolyte's voltammogram, loaded into the memory of the system;
- to store a signal at the primary recording, optimize the conditions of recording a voltammogram and carry out the secondary under optimal conditions;
- to couple the device's performance with the pulser operating, controlled by a complex program, including, for example, in case of employing a standard mercury electrode, such a procedures as washing the electrode, suspending a mercury drop, switching on mixing, switching off mixing, waiting for settling down the solution after recording a voltammogram in the solution analysed as many times as it's required, washing the electrode system, feeding a new solution and repeating procedures;
- to perform an automatic record of the original conditions and the experimental results.

This applications of programmed controls in the above systems may embrace quite a wide range, which makes it possible to supervise the conditions of the experiment, indicate various depolarizers, employ all kinds of operating electrode designs, subject surface areas of hard electrodes to a complex electrochemical treatment, change the data processing program in agreement with the arising necessity, etc.

Most of the tasks set may be solved by means of analogue circuits just like till recently it has been exercised in voltammetric concentration meters of continuous action. But even at the state-of-the art integration of the element base electrical circuits for automatic polarographs operating in the simplest modes, still remain to be rather intricate. In this connection the use of microprocessor facilities and electronic computers

is a significant occurrence in the field of designing automatic polarographic equipment.

There are stages of automatization of modern polarographic systems: internal automatization by means of analog and digital technologies, the automatization of the instruments by means of microprocessors and digital automation with respective software and the automatization in accordance with a principle of the expert systems ensuring recognition of chemical species.

HEAVY METALS IN SEDIMENTS OF THE GULF OF RIGA IN 1994

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In all seasons of 1994 the samples of sediment have been sampled in area where is high sedimentational rate: a coastal zone off the mouth of the Daugava river and in the central deep and also in area with rich benthos.

Cu, Zn, Cd and Pb have been determined with flame AAS and Hg - without flame AAS.

Changes of the metal concentrations have been analysed in different seasons (spring, summer autumn) in one area, have been compared in different area and down on the core of sediments.

ACIDITY AND ION COMPOSITION OF ATMOSPHERIC AEROSOLS AND PRECIPITATION IN NOVOSIBIRSK REGION

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An investigation of ion composition of atmospheric aerosol and wet deposition has received wide acceptance in connection with problems of "acidic precipitation" or, in a more comprehensive sense, problems of formation, transformation and transference of atmospheric components and its action on the terrestrial and water ecosystems [1-3]. Unfortunately, vast expanses of Siberia are scantily known, that plagues a consideration of its contribution to global processes

The goal of our studies was a monitoring of acidity and ion composition of rain, snow and aerosol samples in Novosibirsk region as well improvements in the analytical methodics with instrumentally based methods.

Procedures of sampling and analysis of the rain and snow samples are generally discussed in [1, 2]. A peculiarity of this type of samples is their unstability and so the determinations of a number indeces can be carried out at once after sampling. We used: a portable general-purpose ionometer-conductometer "ANION-210" (for determination of pH, $[\text{Na}^+]$, $[\text{NH}_4^+]$, $[\text{K}^+]$ with ion-selective electrodes and common Ag-AgCl reference electrode filled by analysed sample and for determination of $[\text{HCO}_3^-]$ by potentiometric titration); a portable ion chromatograph ChPI (for determination of $[\text{F}^-]$, $[\text{Cl}^-]$, $[\text{NO}_3^-]$ and $[\text{SO}_4^{2-}]$ and a conductometer 5711 "ELWFO" (for measuring of specific electric conductivity κ_{exp} and conductometric titration $[\text{Ca}^{2+} + \text{Mg}^{2+}]$). Rain samples were analysed just after the rainfall, snow samples were studied after thawing in a stationary laboratory.

The data of analysis were used to calculate the balance of ΣAn anions and ΣKat cations as well as \mathcal{M}_{calc} . The discrepancy between ΣAn and ΣKat was no more than 15 %, and between \mathcal{M}_{exp} and \mathcal{M}_{calc} no more than 20 %. This testifies to the fact that the ions analysed are the main fractions of the ion composition of wet precipitation.

Aerosol sampling was performed using FA-CA filters. Volumetric rate was 6 m³/h, sampling time was 24 h. After exposition a part of the filter was placed in deionised water (5 cm³) for 24 h. The concentration of F⁻, Cl⁻, NO₃⁻ and SO₄²⁻ were determined using an ion chromatograph (sorbet HIKS-1, carbonate eluent, conductometric detector). The results of analysis (with regard to a blank sample) were calculated for 1 m³ of air.

Presented studies are a part of a complex project "Siberian Aerosols" [4] and continue the studies of the ion composition of aerosols performed by us in 1992 in the Novosibirsk region [5]. In summer and winter 1994-1995 the observations were carried out at the following sites: Site #1 near lake Chany, 400 km to the West from Novosibirsk; Site #2 near village Zavyalovo, 90 km to the South-South-West from Novosibirsk; Site #3 near Akademgorodok, 30 km to the South-South-East from Novosibirsk; Site #3a for a distance of 10 km from Site #3 in a direction of decreasing of the pollutants exposure. Site 1 is situated in steppe, and Site 2 is situated in forest. The observation reflected the processes on a regional scale.

For 27 rain samples (June - September 1994, Site 2) the values of pH varied from 4.5 to 7.2 for 32 snow samples (11.94 - 02.95) these varied from 4.65 to 7.37 and the mean values were 5.53 and 5.76, respectively, which coincides with the pH value of 5.6 calculated for the equilibrium of distilled water with CO₂ in air. This indicates to the absence of constant factors of "acidification" or "basification" of precipitation at observation sites. For the mean rain mineralization of 7.5 mg dm⁻³, NH₄⁺ and SO₄²⁻ dominate (their sum is about 36 % from all ions), the fraction of (Na⁺ + Cl⁻) ~27 % (Table 1). In snow (Sites 2,3) summary mineralization Σu is 2 times larger, a fraction of Na increases up to 30-39 % and that of (Ca²⁺ + Mg²⁺) decreases. It is felt that the seasonal dynamics of ionic composition of wet deposition are due to such processes as photochemical reaction, local soil erosion and far atmospheric transference from region near Aral Sea. The distribution of anions in aerosols (Table 2) testifies to a higher stability of the factors of the formation of aerosol composition in which SO₄²⁻ dominates.

Table 1. Ionic composition of wet deposition (numerator in mg dm⁻³) in Sites #2,3 and share (denominator in % eqv.) of main anions in aerosol.

Data	Sites	n	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	ΣAn
06.94	1	14	<u>0.04</u>	<u>0.07</u>	<u>0.11</u>	<u>1.08</u>	1.30
			7.7	7.5	6.2	78.8	
07.94	2	15	<u>0.05</u>	<u>0.09</u>	<u>0.16</u>	<u>1.75</u>	2.05
			6.1	6.1	5.8	82.0	
08.94	2	9	<u>0.04</u>	<u>0.06</u>	<u>0.11</u>	<u>1.24</u>	1.45
			6.7	6.7	6.5	80.1	
09.94	2	8	<u>0.014</u>	<u>0.04</u>	<u>0.12</u>	<u>1.57</u>	1.74
			3.2	3.7	4.6	88.3	
01.95	3	13	<u>0.24</u>	<u>0.36</u>	<u>3.80</u>	<u>10.53</u>	14.93
			4.1	3.3	20.2	72.4	
01.95	3a	13	<u>0.09</u>	<u>0.10</u>	<u>1.47</u>	<u>4.69</u>	6.35
			3.5	2.2	18.5	75.8	

The mean content of ΣAn in continental aerosols is 3.2 mkg m⁻³ [6]. For Site #1 in June this value was 1.3; for Site #2 it was 2.0, 1.3, 1.7 in July, August, September, for Site #3 6.3 ug m⁻³ in January, respectively. This testifies to unimportance of such local factors as soil erosion and anthropogenic contamination at these "background" sites of the Novosibirsk region.

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MACOMA BALTICA AS A BIOTRACER BY MONITORING PETROLEUM POLLUTION OF THE NORTHERN COASTAL SEA OF ESTONIA

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Because of small water volume and high population density of coastal areas petroleum pollution of the Baltic Sea exceeds values for the world ocean [1]. One of its most endangered areas in this respect is the Gulf of Finland with three big harbour cities - Sankt-Petersburg, Helsinki and Tallinn on its shores. Dangerousness is even increased by intensive oil transport and by addition of petroleum-like pollution with wastes of Kohtla-Järve oil-shale processing industry. Molluscs as petroleum pollution indicators compared with other compartments of marine ecosystem have several advantages:

- 1) they are sessile
- 2) they are internationally used for this purpose
- 3) because of underdevelopment of their hydrocarbon metabolism system elimination of hydrocarbon from their body tissues is a slow process ensuring high accumulation levels
- 4) the deposit-feeder *Macoma baltica* has been used for evaluation of petroleum pollution also of other areas of the Baltic [2-4].

In the present work for the assessment of petroleum pollution of different regions of the northern coastal sea of Estonia *Macoma baltica* was used as a biotracer mainly because it is spread over all the investigated region including low-salinity eastern part of the Gulf of Finland.

The results showed that no equivocal direction of concentration changes in dependence on shell size was observed. Concentrations in the Tallinn Bay exceed concentrations in less polluted areas of the Gulf by over 20 times. Second polluted sampling area was Kakumäe in the neighborhood of the Tallinn Bay what is also influenced by ship traffic and by waste discharges of town Tallinn. Petroleum hydrocarbons levels were the lowest in the Central part of the Gulf of Finland, in the

vicinity of Osmussaar and in the Kunda Bay. Moderately elevated concentrations were measured in *Macoma* from the Narva Bay from the areas bordering northeastern industrial region of Estonia (Saka, Purtse rivermouth) and from Klooga area.

From the point of view of possible pollution of the Gulf of Finland of utmost concern is the region of northeastern Estonia from where a great part of pollution coming from Estonia territory into the Gulf of Finland originates: in this area oil-shale processing plants in Kohtla-Järve and Kiviõli, metal and chemistry plant in Sillamäe and thermal power plants are situated. If adding domestic wastes of the towns Narva, Sillamäe and Kohtla-Järve and inflows *via* rivers Narva, Purtse and Pühajõgi it makes it even more dangerous for the ecosystem of the Gulf of Finland. Only partly purified wastes of oil shale processing industry, rich in aromatic structures, pass out through the Purtse river and Saka outlet to the Gulf. These circumstances made this region of special interest for this study. But the analyses showed, that *Macoma baltica* samples taken from these areas did not show a very high petroleum hydrocarbons concentrations. In the region where the Purtse river flows into the Gulf samples were taken 1.5 km westward and 1.5 km eastward from the rivermouth. The mean concentration of petroleum hydrocarbons in *Macoma* from this area were moderately elevated compared with the central part of the Gulf of Finland.

By the data of the present study the investigated region can be divided into three concentration levels group: 1 - the vicinity of Tallinn, including Kakukäe, 2 - Klooga, Narva-Jõesuu, Saka, Purtse and 3 - Central part of the Gulf of Finland, vicinity of Osmussaar, Kunda and Vergi areas.

Conclusions

1. Using mollusc *Macoma baltica* as a petroleum pollution indicator organism it was possible to determine concentration gradients in the northern coastal sea of Estonia: concentrations were higher in areas with higher frequency of shipping traffic and in the vicinity of urbanized areas. In the Tallinn Bay the relevant concentrations were about 20 times higher than in less polluted coastal regions (Kunda, Vergi) or in the central part of the Gulf of Finland.

2. The most probable reason for this gradient is diffuse pollution from different sources like waste discharges, shipping, river inflows etc.

3. Petroleum hydrocarbon concentrations in the neighborhood of Purtse rivermouth, though moderately elevated, are much lower than in the Tallinn region. Obviously a rather rapid decrease of the pollution occurs: lipophilic hydrocarbons are bound to particulate matter and settled down not far from the rivermouth.

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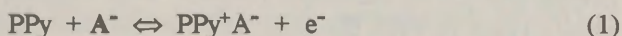
POLYPYRROLE – NOVEL ION SENSITIVE MATERIAL?

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Electrodes modified with conductive polymers, particularly with polypyrrole (PPy), have been characterized as possible potentiometric sensors for the determination of various ions [1-3] and molecules [4]. The electrochemical oxidation of PPy is accompanied by the insertion of anions into the polymer matrix to compensate its positive charge:



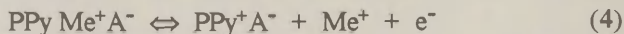
According to the PPy redox reaction the potential of the metal electrode modified with PPy may be expressed by equation

$$E = E_0 + (RT/F) \ln[a_{\text{ox}} / a_{\text{red}} a_{\text{an}}] \quad (2)$$

where a_{ox} , a_{red} are the activities of oxidized and reduced form of PPy. If the doping level of the polymer remains almost constant (i.e. $a_{\text{ox}}/a_{\text{red}} \approx \text{const}$) the following relation is valid:

$$E = E_0 - (RT/F) \ln [a_{\text{an}}] \quad (3)$$

In several reports, a Nernstian potential response of PPy electrode to anions in aqueous [1-3, 5-8] and nonaqueous solutions is obtained [5]. In some cases the anions are trapped into polymer film and redox equilibrium between polymer and solution is established by the movement of cations. The latter process takes place in the case of big organic dopant[9], but also in thick PPy films doped with inorganic anions [5]. In the case of the redox transition of PPy only with cationic exchange



the potential of PPy electrode may be expressed by equation

$$E = E_o + (RT/F) \ln [a_{\text{ox}} a_{\text{cat}} / a_{\text{red}}] \quad (5)$$

and again assuming that doping level of the PPy is approximately const:

$$E = E_o + (RT/F) \ln [a_{\text{cat}}] \quad (6)$$

In the present paper the potentiometric behaviour of PPy films doped with various anions has reported in order to characterize the perspective of PPy as ion sensitive material.

Pyrrole (Fluka) used for synthesis of PPy was purified by distillation over calcium hydride under vacuum and stored in the dark under Ar atmosphere at low temperature. All salts used were analytical reagent grade. PPy films were synthesized potentiostatically ($E = 0.7 - 0.8$ V vs. sat. Ag/AgCl) from Ar saturated aqueous solutions of 0.1 M pyrrole and 0.1 M electrolyte (NaNO_3 , KCl, Cs_2SO_4 , Na_2SO_4 , Li_2SO_4 , MgSO_4) onto Pt. Film thickness d (2 - 60 μm) was regulated by the electropolymerization charge according to the relation 0.4 C/cm² per 1 μm [10]. A conventional three-compartment cell equipped with a Pt wire as counter electrode and a saturated Ag/AgCl electrode as reference electrode were employed for electrochemical polymerization. The working electrodes were in the form of Pt wire (0.1 cm²).

The electrochemical polymerization of pyrrole were performed potentiostatically. The polymerization charge were measured by coulometer. The potentiometric measurements were carried out using a dynamic condensator electrometer. The preceding conditioning of each electrode was performed in separate test-tubes with 5 ml of solution of different electrolytes and concentrations. Film conditioning and potentiometric measurements were carried out at room temperature and in the presence of air.

The composition of the PPy films (10 μm) deposited on Pt wire was examined by electron probe microanalysis (EPMA) using an JSM-35CF (JEOL Ltd., Japan) equipment supplied with two crystal spectrometer and with an energy dispersive spectrometer 860 Series 2 (Link Systems Ltd., England).

For the comparison of the potentiometric behaviour of PPy electrodes and liquid-membrane ion selective electrodes, the nitrate

electrodes based on poly(vinylchloride) (PVC) membrane were prepared. Tris(bathophenanthroline)nickel(II) nitrate as ion exchanger dissolved in *o*-nitrophenyl octyl ether was used.

As a rule the stable potential E does not set up immediately after immersion of the as-prepared PPy electrode into the electrolyte solution. E changes in time while the nature and the rate of change depend on several factors: film thickness, the nature of dopant ion and conditioning solution. The conditioning of electrode is necessary for the stabilization of E . It is a long-time process during which the side products of the polymerization reaction (H^+ ions, pyrrole oligomers etc.) diffuse out from the film, the film pores fill with the conditioning solution and the quasi-equilibrium between PPy electrode and solution establishes. The many-fold change of the conditioning solution accelerates the set-up of the quasi-equilibrium potential E_r . In the experiments described below the PPy electrodes were conditioned with many-fold change of the solution. The rate of the E_r set-up depends essentially upon film thickness. So, for PPy/ NO_3 ($d = 2 - 3 \mu m$) 10 hours is sufficient, but PPy/ NO_3 ($d = 60 \mu m$) needs 150 hours. The electrochemical properties of PPy films do not remain constant during the conditioning. The long-time conditioning decreases the PPy/ NO_3 film redox activity and changes the kinetics of the redox process (the shift of the reduction peak potential $\approx 0.35V$ in negative direction).

The established E_r value depends upon the film thickness and the activity a_c of the conditioning solution (Figure 1). The slope of dependences of E_r on $\lg a_c$ for PPy electrodes conditioned in the solutions of sulphates has positive value and for electrodes conditioned in other electrolytes negative value. In all cases the absolute values of the slope are lower than the Nernstian slope. The final potential value of the PPy electrode after conditioning is not sensitive to the nature of ambient gas (O_2 , Ar) dissolved in the solution, unlikely to the potential values before conditioning. The established E_r is constant for a long-time period.

When the PPy electrode conditioned in certain electrolyte ($E = E_{r,1}$) is shortly exposed in the other solution differing from the conditioning solution only in electrolyte activity the stationary potential E sets up which differs from $E_{r,2}$ acquired after long-time conditioning in the new solution. The set-up of E (short-time response) depends on many factors and was previously studied in [6]. PPy electrodes synthesized and conditioned in solutions of various electrolytes can represent, depending

on the nature of the electrolyte, both anion sensitivity (NaCSN^* , NaNO_3 , KCl , NaF^*) and cation sensitivity (Cs_2SO_4 (Figure 2), Na_2SO_4 , Li_2SO_4). The most important factor in the determination of the short-time response direction and its value is the nature of conditioning solution. Thus, the PPy electrode synthesized in the solution of NaNO_3 but conditioned in the solution of Cs_2SO_4 is cation sensitive and vice versa.

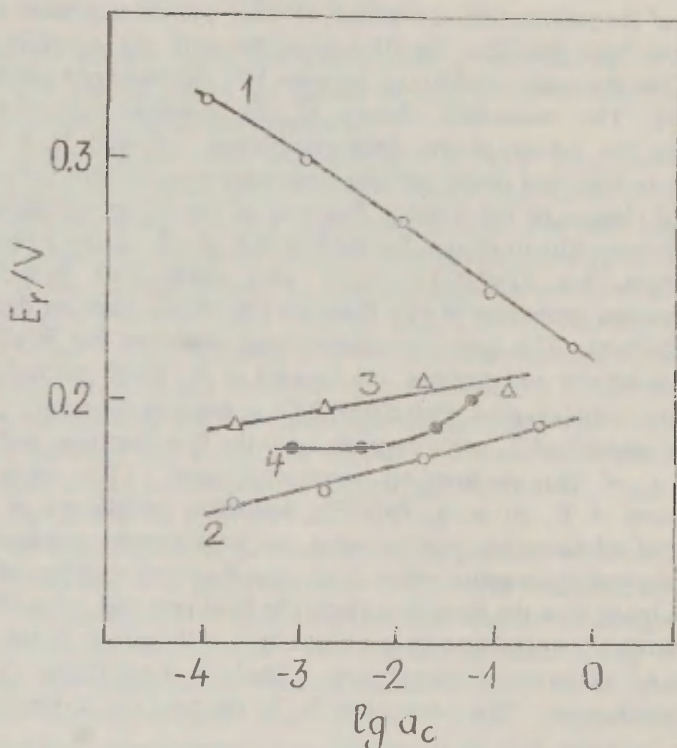


Figure 1. The dependence of the quasi-equilibrium potential E_r of the PPy (30 μm) electrodes on the electrolyte activity a_c of the conditioning solution: (1) NaNO_3 ; (2) Cs_2SO_4 ; (3) Li_2SO_4 ; (4) MgSO_4). The PPy films were synthesized from the 0.1M solutions of the same electrolytes.

* NaCNS and NaF solutions were used only as conditioning. The films were synthesized in 0.1 M NaNO_3 .

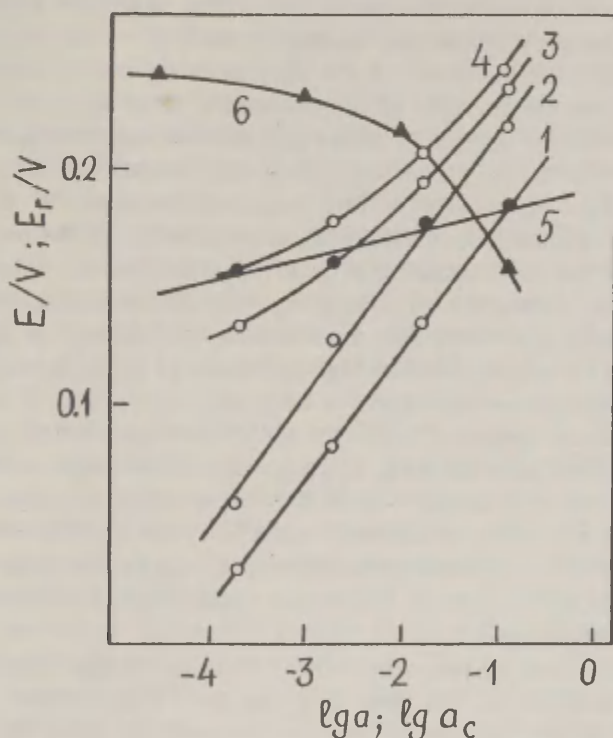


Figure 2. The dependence of the potential short-time response E on the Cs^+ activity a for nontreated PPy electrodes conditioned in the Cs_2SO_4 solutions with different concentrations (M); (1) 0.1; (2) 0.01; (3) 0.001; (4) 0.0001. (5) the dependence of the quasi-equilibrium potential E_r on the Cs^+ activity a_c on the conditioning solution. (6) the dependence of the short-time response E at $a = 0.1$ on the Cs^+ activity a_c in the conditioning solution. The PPy films were synthesized from 0.1 M Cs_2SO_4 .

The length of the linear part of the E - $\lg a$ relationship depends on the concentration of the conditioning solution. There are two types of deviation from the linear relationship for anion sensitive PPy electrodes. The deviation at low concentration is similar to the one obtained in the

case of anion selective PVC membrane electrodes (related to the dissolving and dissociation of the ion exchanger in the test solution). This deviation increases by increase of a_c . If a_c is low ($< 10^{-3}$), the deviation takes place also at high concentrations ($10^{-2} - 1$ M). Both kind of deviations are connected with the reconditioning of PPy electrode. Deviation from the linearity of dependences of E on $\lg a$ for cation sensitive electrodes (Figure 2) occurs only at low concentrations after conditioning in the dilute solutions of sulfates and is not related to reconditioning. Most likely at low cation concentration the role of transport of sulphate anions become more remarkable and the potential jump on the polymer/measuring solution interface becomes influenced also by anion concentration. The long-time and short-time responses of PPy electrodes conditioned in the solutions of $MgSO_4$ are almost independent on concentration of $MgSO_4$ (Figure 1, plot 4). In this case mobility of both anions and cations is restricted.

The absolute values of the slopes of the linear part of E - $\lg a$ plots are greater than those of E - $\lg a_c$ plots and are decreased when the thickness of the PPy film $d < 10 \mu m$. The values of the slope for anion sensitive PPy electrodes (conditioned in $NaCSN$, $NaNO_3$, KCl , NaF) are $-50 \div -58 mV$ and cation sensitive electrodes (conditioned in Cs_2SO_4 , Na_2SO_4 , Li_2SO_4) $50 \div 56 mV$, for divalent cations (Ni^{2+} , Ca^{2+}) the slope is $10 \div 30 mV$ per decade.

Special measurements were carried out to determine influence of pH of the solution on the short-time response of the PPy modified electrodes. It was established that in the case of anion sensitive electrodes if the thickness of the PPy film is over $5 \mu m$ the potential is almost independent of the pH value in the interval of $pH 4 \div 7$. The pH function of cation sensitive PPy electrode (E increases with the decreasing of pH) is more remarkable but the linear correlation between this short time response and pH is absent.

It was established that the short-time response of anion sensitive PPy electrodes to the change of the electrolyte activity is not sensitive relative to the cation nature. The change of E caused by the influence of the cation nature at the same concentration of electrolyte is connected only with the change of the activity coefficients of the anion. On the other hand, the response of the cation sensitive PPy electrodes is also influenced by the anion nature. Thus, the difference of E of the PPy electrode conditioned in $0,1$ M Cs_2SO_4 and immersed in the solutions of Cs_2SO_4 and $CsNO_3$ with approximately equal $a_{Cs^+} = 0.1$ is $-30 mV$. The

influence of anions decreases in the following sequence: $I^- \approx Br^- \approx NO_3^- > Cl^- \approx ClO_4^- > F^-$. The sensitivity increasing of the cation sensitive PPy electrode respect to anions leads to the decreasing of the slope of the short-time response. The Nernstian cationic response was obtained only in the solutions of the electrolyte with highly hydrated anion (sulphate).

The influence of the interfering inorganic anions on the potentiometric behaviour of anion sensitive PPy electrodes is rather complicated. The studied ions can be divided into two groups. To the first group belong the anions which can not easily insert into the polymer film and redope the PPy. The typical representative of this group is sulphate ion. To the second group belong all other ions studied. They are able to exchange the dopant anions in the polymer film quite rapidly and the redoping process starts immediately after immersion of the electrode into new solution. So, according to the EPMA data the PPy ($d = 10 \mu m$) electrode conditioned in 0.1 M solution of KCl practically does not redope with sulphate during the soaking of 5 minutes in 0.1 M K_2SO_4 . At the same time in 0.1 M solution of KBr more than a half of Cl^- ions were replaced by Br^- ions. In connection with intensive redoping process in some cases the potential changes continuously and determination of the short-time response is complicated. Nevertheless we tried to determine the selectivity coefficients k according to the potential values at once after immersion in the new solution. We have used measuring both in mixed solutions and in separate solutions. The choice of interfering ions was limited by additional condition: the electrolyte solution pH should be within the interval 5 - 7. The calculated k are independent of the polymer layer thickness. From the Tables 1 and 2 one can see, that the short-time response of PPy electrodes is generally non-selective. The k values of all PPy electrodes are relatively high excepted the divalent ions as interfering ions. Particularly low k have all anion sensitive PPy electrode in respect to sulphate. The changes of k values at the same interfering ions and at the same potential determining ion respectively, with some exceptions, generally follows the Hofmeister lyophilic series [11]: CNS^- , I^- , ClO_4^- , NO_3^- , Br^- , Cl^- , F^- , SO_4^- for anions and Cs^+ , Rb^+ , K^+ , Na^+ , Li^+ , Mg^{++} for cations which are based on the differences of the solvation energies. The interfering effect of ions is the greater the less lyophilic is the interfering ion and the interfering effect of one concrete ion is the smaller the less lyophilic is the potential determining ion. As appears from Table 1, the series of anions by their interfering influence for the PPy electrode conditioned in $NaNO_3$ and for nitrate selective

electrode with a liquid membrane are with some exceptions (F^- , ClO_4^-) generally similar.

Table 1. The selectivity coefficients of anion sensitive PPy electrodes.

Interfering anion	Solution of conditioning of PPy electrode				PVC membrane NO_3^- selective electrode
	10^{-2} M NaCNS	0.1 M $NaNO_3$	0.1 M KCl	0.1 M NaF	
CNS^-	*	1.3	-	-	-
I^-	$2 \cdot 10^{-1}$	0.5	2.8	5.1	30
ClO_4^-	$8 \cdot 10^{-2}$	0.2	1.3	1.9	$2.4 \cdot 10^3$
NO_3^-	$8 \cdot 10^{-1}$	*	1.8	16	*
Br^-	$1 \cdot 10^{-1}$	0.4	1.6	4.9	$2 \cdot 10^{-1}$
Cl^-	$1 \cdot 10^{-1}$	0.3	*	3.6	$7 \cdot 10^{-3}$
F^-	$6 \cdot 10^{-2}$	0.2	-	*	$1 \cdot 10^{-3}$
SO_4^-	$7 \cdot 10^{-3}$	$6 \cdot 10^{-3}$	$8 \cdot 10^{-2}$	$7 \cdot 10^{-3}$	$1 \cdot 10^{-3}$

Table 1. The selectivity coefficients of cation sensitive PPy electrodes.

Interfering cation	Solution of conditioning	
	0.1 M Cs_2SO_4	0.1 M Li_2SO_4
Cs^+	*	5.0
Rb^+	$7 \cdot 10^{-1}$	3.4
K^+	$6 \cdot 10^{-1}$	2.8
Na^+	$3 \cdot 10^{-1}$	1.6
Li^+	$2 \cdot 10^{-1}$	*
Cd^{++}	$2 \cdot 10^{-2}$	0.7
Ni^{++}	$1 \cdot 10^{-2}$	0.3
Mg^{++}	$1 \cdot 10^{-2}$	0.2

The PPy electrode can be considered as relatively hydrophobic microporous system [12]. There is a lot of deep pores with different dimensions in the polymer, some of these pores may even reach the surface of the metal. After conditioning the pores are filled with the

conditioning solution. The PPy electrode is in the redox equilibrium with the solution in its pores. The long-time potentiometric response of the PPy electrode after its reconditioning in the new solution leads to the new redox equilibrium with changed oxidation level of PPy. According to equation (1) and (2) the change of oxidation level leads to the $E_r, \lg a_c$ relationship with low absolute value of the slope.

The most important potential jump determining potentiometric properties of PPy modified electrodes is localized on polymer/solution interface. The polymer/solution interface involves the external surface/solution and internal surface/solution boundary. According to the results of EPMA measurements the mass exchange between the solution in pores and the bulk solution is unexpectedly quick. For instance, no K^+ ions were found in PPy/Cl film (10 μm thick) conditioned in 0.1 M KCl and immersed into water for 1 minute. So, it is reasonable to suppose that during short-time measurements (3 - 5 minutes) the conditioning solution in pores is replaced by bulk solution and the properties of the external surface/solution and internal surface/solution interfaces are similar. The EPMA were also used to determine the rate of exchange of the anions between PPy film and solution. The electrodes conditioned in 0.1 M solution of KCl were immersed for different times into 0.1 M solution of KBr. It was established that during 1 and 5 minutes approximately 30 % and more than 60 % of Cl^- ions were replaced by Br^- ions. So, the exchange rate between dopant anions in the film and ions in the solution is quite high and depends on the nature of anions. One can see from the table 1 that selectivity coefficient of PPy/Cl electrode for Br^- anions is high (1.8), i.e. Br^- ions as less hydrophilic prefer to go into PPy film. Essentially different results were obtained if PPy/Cl electrode was immersed into solution of K_2SO_4 . In this case during 5 minutes only 1% of Cl^- ions are replaced by SO_4^{2-} ions. So, it is possible to conclude that relative low selectivity of PPy electrodes is connected with the high exchange rate between PPy film and solution. Only in the case if the hydrophilicity and mobility of ions which take part in the exchange process are essentially different can be observed remarkable selectivity. So, all ion sensitive PPy electrodes have very low values of k for sulphate anion (Table 1).

Characteristic of the PPy electrodes conditioned in the solutions of sulphates are the very low mobility of dopant anion in the film and existing of the cations electrostatically bound with dopant. Both peculiarities are assured by EPMA data.

The PPy electrode function that arises from the contact of a conditioned electrode with the measuring solution 3 - 4 min. after the electrode immersion (the short-time response) may be interpreted as the potential jump caused by ion moving through the phase boundary PPy/solution without change in the oxidation degree of the bulk polymer. This jump depends both on the activity of the measuring solution and on the activity of the conditioning solution as the measure of the doping degree. The short-time response of the PPy electrode does not remain stable during a long-time contact with the measuring solution due to the reconditioning of the microporous system. Thicker films ($d > 10 \mu\text{m}$) are more stable against reconditioning.

From our results it is clear that the potentiometric function of PPy electrode should be characterized as relatively unstable and non-selective. The PPy films are also sensitive to redox couple in the solution [8] what is the additional interfering factor for the use of PPy as ion sensitive material. Therefore the PPy films doped with inorganic anions have no perspective as ion selective electrodes. PPy electrodes can be used in some cases for the determination of the total salt concentration, for example, water salinity, also as matrix for the fixing of ion sensitive compounds.

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METALLIZED CARBON ELECTRODES FOR ANALYTICAL APPLICATIONS

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Carbon materials have been widely used in various electrochemical applications. The main advantage of carbon electrodes in analytical applications is their low cost and ease of fabrication. For the purpose of utilization in electroanalysis a chemical stability and high electrocatalytic activity of a working electrode are required. In order to achieve a desirable signal-to-noise ratio, it is necessary for the indicating electrode to possess a high electron transfer rate and a low background current. A large variety of carbon materials are employed in electroanalysis: glassy carbon, pyrolytic graphite, graphite rod, carbon paste, carbon fiber, carbon black, carbon film, etc.

The metallization of carbon substrates can be used for the improvement of electrode properties. The purpose of this work was to study the electrocatalytic properties of thin metal films for the development of electrochemical sensors.

Thin films of gold and platinum were produced by vacuum evaporation onto glassy carbon substrate. The oxygen reduction reaction and the electrochemical reactions of hydrogen peroxide were investigated. The electrochemical behavior of thin film gold and platinum electrodes towards oxygen reduction was not much different to that of corresponding bulk electrodes. Voltammetry curves for oxygen reduction at the thin film Au and Pt electrodes show that a diffusion-limiting current plateau is formed in a wide region of potentials. The presence of a current plateau on i, E -curves is favourable for the development of amperometric sensors with good performance characteristics.

Thin film Pt showed a remarkable electrocatalytic activity in the reactions of H_2O_2 in a wide pH range, whereas thin Au film was active in the solutions of high pH. A large group of biosensors is based on the oxidation of enzymatically generated H_2O_2 . Thin film Pt on carbon substrate is a suitable indicating electrode for H_2O_2 -based biosensors.

SOME ASPECTS OF THE APPLICATION OF THE MEMBRANE COVERED AMPEROMETRIC SENSOR

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In order to determine the content of gas in liquids and gaseous phase, the membrane covered amperometric sensors are used. The gas content in the medium under investigation is expressed by units of mg/l, ppm (part per million), the percentage of saturation as well as by units of partial pressure, tension and activity. Not all of these units lack physical meaning. It is not understandable what the oxygen tension or partial pressure in the case of liquids really means. The formal use of different units will cause difficulties in the comparison of the results of experiments in different areas of research and makes harder a deeper understanding of the mechanism of the examined process. This is due to the absence of an unambiguous understanding of the connection of the sensor's output signal with the state of the dissolved gas and the parameters of the medium (for instance the solved gas in the salt solution), i.e. there is no common understanding of how the membrane covered amperometric sensors transform the analytical concentration in the studied media to the output signal and which of the transducers gives physical meaning of measured signal.

The function of the transduction of the amperometric diffusion limited sensor is determined by the dependence between the output signal of the sensor I_d and the concentration of the examined component c_m :

$$I_d = k_f k_d c_m / K_{md} \quad (1)$$

where k_f is the coefficient of the transduction of the diffusion flow to the output current of the sensor, $k_d = A_d D_d / l_d$ is the coefficient of the transduction of the concentration of the gaseous component to the gas flow, A_d , l_d , D_d are area, thickness and coefficient of diffusion of the

diffusion limited layer of the sensor. The coefficient of distribution of the gas between boundary phases K_{md} , i.e. the relation of equilibrium concentrations of the examined gas and the test media c_m and the diffusion limited layer of the sensor c_d can be expressed:

$$K_{md} = c_m/c_d \quad (2)$$

It is shown that in the case of saturation of the test media by the examined gas, the amperometric membrane covered sensor gives the same signal for the environments with different thermodynamic properties (organic liquids, water, salt solutions and others).

For the application of the amperometric sensor, units of effective concentration are used [1]. Effective concentration c_e expresses the summarised effect of the dissolved gas (having thereby different analytical concentration) on the membrane of sensors. The effective concentration is not good enough for the comparison of the results of the measurements in different media and does not give the answer about the physical meaning of quantity c_m/K_{md} , directly affecting the membrane of the sensor.

The equilibrium distribution of the gas component between the phases is attained by means of equal and opposite flows of gas through the boundary interfaced surface:

$$j_{gl} = j_{lg} \quad (3)$$

where $j_{gl} = p_{gl} c_g$ is the equilibrium gas flow density from the gas phase into the liquid phase, $j_{lg} = p_{lg} c_{gl}$ is the equilibrium gas flow density from the liquid phase into the gas phase, p_{gl} and p_{lg} are probability coefficients of the transitions of gas molecules from the gas phase into the liquid phase and vice versa.

As it seen from eq. (3) the coefficient of the distribution of gas between liquid and gas is a function of the probabilities of the transition of gas molecules through the interfacial surface:

$$K_{gl} = c_g/c_{gl} = p_{lg}/p_{gl} \quad (4)$$

where c_g and c_{gl} denote the concentrations of the gas component in the gas and liquid phases.

The change of the state of molecules by transition from one phase to another is connected with the change of energy. Therefore, the distribution coefficient can be determined also as a function of the change of the state through the change of energy $\Delta\bar{w}$. For the determination of the form of function $K = f(\Delta\bar{w})$, we can examine equilibrated heterogeneous system of gas-liquid-solid matter.

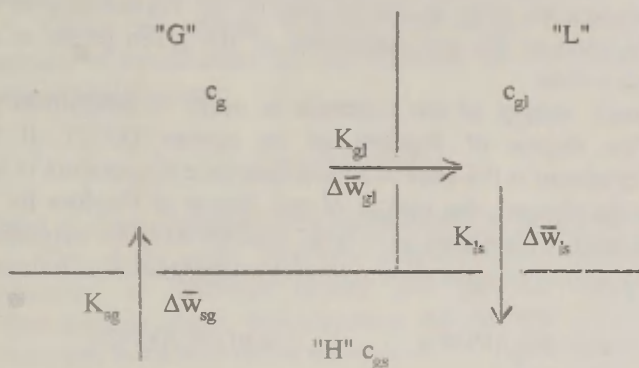


Figure 1 Model of the equilibrium distribution in heterogeneous system "G" - gas, "L" - liquid, "S" - solid matter, K_{gl} , K_{ls} , K_{sg} - coefficients of distribution; $\Delta\bar{w}_{gl}$, $\Delta\bar{w}_{ls}$, $\Delta\bar{w}_{sg}$ - change of the energy of the state.

The coefficient of the distributions at the given heterogeneous system can be given as:

$$K_{gl} = c_g/c_{gl}, \quad K_{ls} = c_{gl}/c_{gs}, \quad K_{sg} = c_{gs}/c_g \quad (5, 6, 7)$$

From the equations (5, 6, 7) it follows that a multiplied dependence exists between the coefficients of distributions:

$$K_{gl} K_{ls} K_{sg} = 1 \quad (8)$$

It follows from the law of the conservation of energy that the sum of the changes of the energy of the state of molecules by consecutive transition of gas molecules by phases "G" \rightarrow "L" \rightarrow "S" \rightarrow "G" is equal to zero:

$$\Delta\bar{w}_{gl} + \Delta\bar{w}_{ls} + \Delta\bar{w}_{sg} = 0 \quad (9)$$

The system of equations (8), (9) satisfies the exponential form of function $K = f(\Delta\bar{w})$:

$$K_{gl} = \exp(\alpha\Delta\bar{w}_{gl}), \quad K_{ls} = \exp(\alpha\Delta\bar{w}_{ls}), \quad K_{sg} = \exp(\alpha\Delta\bar{w}_{sg}), \quad (10,11,12)$$

where α is the coefficient of the dependence of the probability of the interfacial transition of gas molecules from the change of energy of the state by transition. Coefficient α by its physical meaning must be a quantity of energy, by what as can be used by the normalizing of the energy of the state of the gas component of the given phase of the heterogeneous system.

The kinetic energy of the molecule as usual is normalized per energy of the degree of freedom of its motion ($kT/2$). If the heterogeneous system is the state of equilibrium (the temperature is also the same in the phases), the energy of one degree of freedom for all phases is the same. This allows us to offer quantity $kT/2$ for normalized coefficient α and we can write the coefficient of distribution as follows:

$$K_{gl} = \exp\{\Delta\bar{w}_{gl}/(kT/2)\}, \quad K_{ls} = \exp\{\Delta\bar{w}_{ls}/(kT/2)\},$$

$$K_{sg} = \exp\{\Delta\bar{w}_{sg}/(kT/2)\} \quad (13, 14, 15)$$

In the case of the membrane covered oxygen sensor, the coefficient of the distribution of gas between the media under investigation and the sensors membrane can be expressed:

$$K_{md} = \exp\{\Delta\bar{w}_{md}/(kT/2)\} \quad (16)$$

From the equations (1, 4, 16) we get the expressions:

$$c_m/c_d = p_{dm}/p_{md} = \exp\{\Delta\bar{w}_{md}/(kT/2)\} \quad (17)$$

A result of the function of transduction can be expressed:

$$I_d = k_f k_d (p_{md}/p_{dm}) c_m \quad (18)$$

where $p_{dm}/p_{md} = \exp\{-\Delta\bar{w}_{md}/(kT/2)\}$ equals to the reciprocal of the coefficient of distribution k_{md} .

The concentration of the examined gas component c_m is transduced to the boundary of the phases between the examined media and the

diffusion limited layer to the equilibrium concentration c_d at the surface layer of the membrane. The interfacial boundary will act as a probability transducer of the concentration of the gas component and its function of transduction can be expressed

$$c_d = k_p c_m \quad (19)$$

where $k_p = p_{dm}/p_{md} = 1/K_{md}$ is the coefficient of the interfacial transduction of the concentration of gas the component.

Taking into account equation (19) we get the expression of the function of transduction for the diffusion limited membrane covered amperometric sensor

$$I_d = k_f k_d k_p c_m \quad (20)$$

where all steps of transduction are expressed by their own coefficients.

The above given approach characterizes the state of the gas component in different phases and permits us to widen the comprehension about determination the content of the soluble gas component by the membrane sensors.

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MICROCOLUMN HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY FOR ANALYSIS OF ENVIRONMENTAL POLLUTANTS: POLYAROMATIC HYDROCARBONS, PHENOLS

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High-performance liquid chromatography (HPLC) is one of the most convenient and modern analytical methods. Microcolumn HPLC has become more commonly used for environmental analysis. This analytical method enables to reach high efficiency of separation of compounds even at the case of isocratic elution. Another advantage of this method is comparatively low (15 - 25 times lower than in ordinary HPLC) expenditure of elution solvents. The experience of application of microcolumn HPLC for analysis of two group of environmental pollutants (PHH and phenols) is generalized.

Phenols. Phenols are also listed by USA EPA as priority pollutants [1]. The water contamination by phenols can be high in some regions of Estonia, as the oil shale industry is producing a huge amounts of phenols containing wastewaters that are discharged to some rivers and Gulf of Finland. Colorimetric methods are still widely used for determination of phenols besides of the fact that their accuracy is very low. HPLC can be alternative improved method for phenol analysis. Microcolumn HPLC has been used for determination of individual phenols and chlorophenols. The equipment used was chromatograph "Millichrom-1" ("Nauchpribor", USSR) with UV-spectrophotometer (190 - 360 nm). 64 x 2 mm reversed-phase column packed with Separon C18 ("Chemapol", Czechoslovakia) was applied. For analysis of phenol and substituted phenols the isocartic elution with mobile phase containing 45% acetonitrile in water (HPLC grade) and flow rate 50 $\mu\text{l min}^{-1}$ was

used. Phenols were detected at 280 nm. The analytical method has been applied for determination of phenol and substituted phenols in the wastewaters of oil shale thermal treatment and in the water of some rivers (see Table 1).

Table 1. Concentration of phenols in water samples from Estonian oil shale region, mg/l.

Phenols	Purtse River	Leachate from ash dump, Kohtla-Järve	Kohtla-Järve Central Wastewater Treatment Plant, influent	Kohtla-Järve Central Wastewater Treatment Plant, effluent
Resorcinol	0.0136	14.6	0.3	0.14
5-Methylresorcinol	0.020	18.6	0.5	-
Phenol	0.0007	98.4	0.87	0.03
m-Cresol+p-Cresol	0.0011	43	0.47	0.04
o-Cresol	0.0013	18	0.19	-
3,4-Dimethylphenol	-	17.6	0.06	0.025
2,3-Dimethylphenol+	0.0006	113	0.103	0.03
2,5-Dimethylphenol				
2,6-Dimethylphenol	0.0006	106	0.06	-

The same chromatograph has been used for analysis of chlorophenols. The mobile phase was a mixture of 50 % acetonitrile and 0.2 % acetic acid in water with flow rate 100 μ l/min. Wavelength used for detection was 230 nm. The corresponding retention times (in minutes) were: o-chlorophenol - 3.2; p-chlorophenol - 3.6; 2,4-dichlorophenol - 4.8; 2,4,6-trichlorophenol - 7.8; 2,3,4,6-tetrachlorophenol - 9.5; pentachlorophenol - 14.5.

Detection limit for the method without concentration of samples is about 0.01 mg/l of individual phenols. The extraction procedure with methyl ether or some other solvent can be used for concentration of the samples if necessary.

Table 2. PAH content in different environmental samples (* $\mu\text{g/l}$ or $\mu\text{g/kg}$ dry weight).

PAH	*Snowmelt , (Tallinn, Hirvepark)	Lichen <i>Hypogymnia physodes</i> (Tipu)	Alga <i>Enteromorpha intestinalis</i> (Tallinn Bay)	Bottom sediments (Vääna Bay)	Fly ash (Kohtla- Järve Powerplant)	Soil (Lagedi village)	*Leachate from ash dump Kohtla-Järve	Bottom sediments (Purtse River)
Phenanthrene	1030	146	31.1	15.6	85.7	44.8	2.56	7.7
Anthracene	419	5.9	0.94	0.28	4.2	3.3	0.75	2.4
Fluoranthrene	549	113	16.4	6.6	68.7	178	7.0	23.7
Pyrene	2190	45.2	7.9	2.1	112.5	60	39.4	45.3
Benzo(a)anthracene	306	27.9	7.0	2.35	92.1	121	0.78	50.6
Chrysene	177	32.3	12.9	1.3	138	122	1.41	55.6
Benzo(b)fluoranthene +benzo(e)pyrene	519	15.4	-	0.28	461	85	0.07	124
Benzo(k)fluoranthene	567	7.7	-	-	11.6	67	0.11	125
Benzo(a)pyrene	519	6.5	0.69	0.31	15.7	121	0.13	440
Dibenzo(ah)- anthracene	-	-	-	-	-	305	0.30	9
Dibenzo(ac)- anthracene	-	-	-	-	56.7	-	-	26
Benzo(ghi)perylene	706	20.1	-	-	77.3	144	0.10	280
Indeno(1,2,3-cd)- pyrene	-	-	-	-	-	56.1	-	-

Polyaromatic hydrocarbons (PAH). PAH are well-known environmental contaminants listed by USA EPA as priority pollutants [1]. Some of them are classified as possible or probable cancerogens [2]. Microcolumn HPLC with fluorimetric detection has been utilized for quantitative determination of PAH in different environmental samples. The water samples have been extracted by n-hexane (0.5 - 4 l of water shaken twice with 30 - 80 ml hexane). The hexane extraction of dry samples (5 - 20 g) of soil, bottom sediments, lichen, fish, dust, etc. has been conducted in Soxhlet during 8 - 10 hours. Recently it has been ascertained that Soxhlet extraction may be successfully replaced by ultrasound extraction at room temperature (22 kHz, 30-80 mL of hexane, during 5 minutes in two steps). Hexane was vapourized from the aliquots of hexane extracts in air. The thin-layer chromatography on aluminium oxide has been used for further fractionating of samples if necessary. For chromatographic determination of PAH the residue was dissolved in 0.2 ml of ethanol. Chromatograph X-1311 (Minsk, Byelorussia) equipped with fluorimetric detector has been applied for quantitative analysis of PAH in hexane extracts. The mixture of acetonitrile-water 93:7 (by volume, HPLC grade) as a mobile phase with flow rate 8 μ l/min was used. The gradient elution improved the separation of PAH somewhat, but even in the isocratic elution the separation of PAH was satisfactory. Two excitation wavelengths (254 nm and 296 nm) with range of registration 330 - 600 nm were used for detection. Chromatographic column (0.5 x 300 mm) was packed with Silosorb C18 ("Chemapol", Czechoslovakia). Utilizing microcolumn HPLC method up to 14 individual PAH have been identified. The sensitivity of this method varied a little bit for different PAH under study and was approximately 2 ng per sample. Coefficient of variation for HPLC method was 1.5 %. The variety of samples analyzed is reflected in data presented in Table 2.

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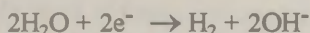
SOME ASPECTS OF ELECTROCHEMICAL TREATMENT OF WATER

P. Vares, J. Tamm

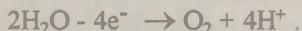
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The electrochemical treatment of water causes essential changes in chemical and physical properties of water and water solutions. Application of this method makes possible to decrease considerably the level of calcium and magnesium ions - to reduce the hardness of water, to prepare desinfective solutions, to purify technological wastewater from waste products.

If a direct current is passed through the water evaluation of hydrogen and generation of hydroxyl ions are the principal products on the cathode



and evaluation of oxygen and generation of hydrogen ions on the anode

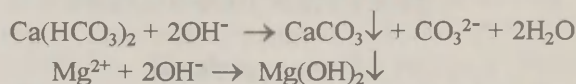


As a result the water in cathode compartment becomes more alkaline and in anode compartment more acidic. The essential changes take place in the redox properties of such water [1]. The electrochemically treated water can be easily produced and stored if anode and cathode compartments are separated by the diaphragm.

The measurements were carried out in flow cell with the diaphragm. The anode was manufactured from titan modified with ruthenium oxide and cathode was manufactured from stainless steel. The composition of the solution, flow rate and the current density I was varied during this study. The pH, redoxpotential and concentration of some ions in water before and after electrolysis were determined.

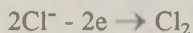
The total content of salt in tap-water before the electrolysis was 0.5 - 0.7 g/dm³ and the content of chloride ions was 0.07 - 0.1 g/dm³. After electrochemical treatment the pH of solution in cathode compartment

increased till 12 and redoxpotential E fall to -0.9 V vers. sat. Ag/AgCl electrode. The content of calcium salts in catolyte fall 40 - 50 times if 10 - 20 kWh/m³ were spended but the fall of content of magnesium salts was essentially less. The processes take place are

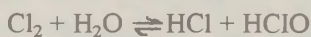


The content of iron and heavy metals also decreased. A little surprising is essential decrease of the content of Ca²⁺ and Mg²⁺ ions in the water of anode compartment. The decrease of the content these ions was 20 - 50 times. This phenomenon is probably connected with migration of cations from anode to cathode compartment during electrolysis. The value of the pH of the water in anode compartment decreases and redoxpotential increases during electrolysis. If the charge passed the cell exceed 500 C/dm³ pH dropped down to 1.5 - 2.5 and E rised to 1.2 - 1.22 V. The total concentration of oxydizin particles c_{ox} in the treated water was below 4·10⁻³ mol/dm³ or 0.15 g/dm³ of molecular chlorine.

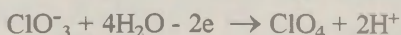
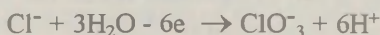
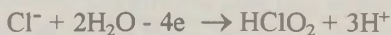
Much more active solutions are possible to produce if to increase the content of chloride ions in solutions (add NaCl). In this case it is possible to produce the solution with content of free chlorine up to 7 g/dm³ and efficiency of the process was quite high (40 - 90 %). The values of pH and E were almost independent of the content of NaCl in solution. The pH of the solutions is approximately 2 and redoxpotential E = 1.18 - 1.22 V. During the electrolysis of water with concentration of chloride ion not very low molecular chlorine is a very important product

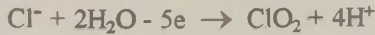
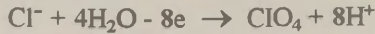


and there are equilibrium process in the solution



But not only these processes are active in this conditions. There are a lot other reactions such as





In some cases hydrogen peroxyde and very active free radical type compounds (H° , HO_2 , O° , OH° , O_2) are in solution [2, 3].

It is evident that experimentally measured redoxpotential is a mixed potential determined by many redoxsystems.

The essential changes take place in the structure of water during electrolysis [4, 5]. Strong electric field specially near the surface of the electrodes and in the pores of the diaphragm lead to break the some part of hydrogen bonds between water molecules and so more or less free water molecules or instable water structures appear in solution. Such structure are able to exist during some time and we have a special very active water. This water has high physiological and chemical activity and can be used as desinfect solution in medicine, food industry and other areas. It is important to emphasize that such kind of water is much more frendly for environment as classical desinfecting agenda such as chloride of lime.

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Co, Ni, Cu AND Zn CONCENTRATION IN HAIR OF CHILDREN OF ESTONIA

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About 20 years the concentration of Pb, Cd, Cu and Zn in body fluids of man has been investigated, but up till now we have no information about Co and Ni concentration in organism [1, 2].

In this study, the level of Co, Ni, Cu and Zn were determined in hair of Estonian children. The samples were collected from 538 boys and 586 girls ages 4 - 15 years, who lived in different industrial and traffic pollutional areas. Also the possible correlation with drinking water was examined.

In recent years human hair has been widely used as biopsy material for trace element status and for monitoring of environmental pollutants. Human hair offers a number of important advantages, compared to blood, serum and urine. The samples can be easily collected, transported and require no special equipment or storage procedures.

From collected hair only the first 3 cm proximal to the scalp were used for analysis. The hair samples were washed with 1 M nitric acid, bidistilled water and dried at 40 °C.

To 0.3 - 0.5 g dry hair samples 5 ml conc. nitric acid was added and mineralized at 180 °C for 6 hours in a tephlo bomb. After cooling the reaction mixture was diluted to 25 ml with bidistilled water.

Determinations of Cu and Zn concentration were performed by way of flame atomic absorption spectrometry (AAS), (Pye-Unicam SP 9-700, and Co and Ni concentrations were performed by way of furnace AAS (Philips PU 9100X).

The statistical analysis was used to find mean, SD, mode and relations between concentrations in hair to find possible correlation with drinking water in Tables 1 - 3.

Table 1. General mean concentration of Cu, Zn, Ni and Co in hair [ug/g].

	Cu	Zn	Ni	Co
Mean	7.79	140.4	1.064	0.066
Min	0.5	77	0.011	0.001
Max	17.9	236	4.689	0.438
Mode	8.18	126	0.596	0.011
SD	2.069	24.44	0.889	0.045
STDev	3.013	32.31	0.135	0.072

Table 2. Mean concentration of Cu, Zn, Ni and Co in different districts [ug/g].

District	Cu	Zn	Ni	Co
Kohtla-Järve	7.61 ± 3.26	129 ± 12.58	0.72 ± 0.78	0.037 ± 0.032
Tallinn	7.98 ± 2.19	144 ± 28.52	0.602 ± 0.541	0.071 ± 0.078
Põlva	7.31 ± 1.92	126 ± 27.82	2.625 ± 1.136	0.046 ± 0.033
Sillamäe	5.61 ± 1.97	130 ± 18.12	0.307 ± 0.204	0.046 ± 0.033
Loo	8.44 ± 1.29	196 ± 33.33	2.28 ± 1.151	0.138 ± 0.087
Haapsalu	9.27 ± 2.93	119 ± 12.47	1.553 ± 1.522	0.087 ± 0.115
Tartu	8.62 ± 5.13	151 ± 32.59	0.901 ± 0.989	0.068 ± 0.067

The mean concentrations of Cu and Zn in the hair were lower compared with the values usually mentioned in literature [3, 4, 5].

The concentration of Co and Ni was also studied. It is a lack of information in the literature about the concentration of Co and Ni in human hair and make no sense to compare our results with them.

Statistical analysis showed that there was no correlation between Co and Ni concentration in human hair and drinking water, low correlation was found between Cu ($r = 0.638$) and Zn ($r = 0.3$). Significantly higher Zn concentration was found in girls hair, and Cu concentration was a few higher in boys hair. No differences were detected in Co and Ni concentration between boys and girls. Age related differences were found in Zn concentrations. Co and Ni concentrations were not related with age (Figure 1 - 4).

Table 3. Concentration of Cu, Zn, Ni, Co in drinking water.

District	Trace metal [mg/l]			
	Cu	Zn	Ni	Co
Loo	0.16	0.17	0.001	0.003
	0.16	0.17	0.001	0.002
	0.16	0.18	0.005	0.004
	0.16	0.17	0.001	0.003
	0.15	0.17	0.003	0.002
Tallinn	0.16	0.18	0.001	0.006
	0.12	0.12	0.001	<0.001
	0.14	0.29	0.003	<0.001
	0.028	0.02	<0.001	0.002
	0.133	0.13	<0.001	<0.001
Tartu	0.04	0.17	<0.001	<0.001
	0.013	0.17	<0.001	0.003
	0.1	0.12	<0.001	0.002
	0.01	0.17	<0.001	<0.001
Põlva	0.01	0.08	0.002	<0.001
	0.012	0.15	0.002	<0.001
	0.011	0.55	0.004	0.002
	0.09	0.11	0.001	<0.001
Kohtla-Järve	1	2.3		
	0.89	2.4		
	1.3	3		
Haapsalu	1	2		
	0.91	1.72		
Mean	0.231	0.515	0.002	0.0029
Mode	0.16	0.17	0.001	0.003
STDev	0.359	0.872	0.001	0.0013

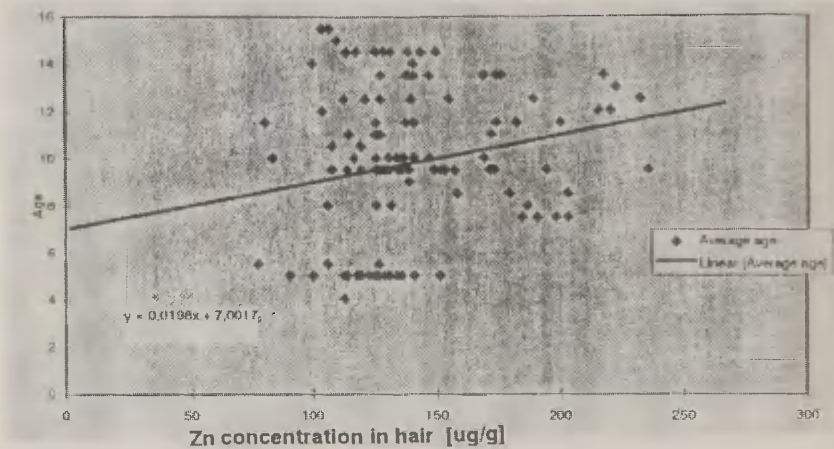


Figure 1. Zn concentration in hair in relation to age

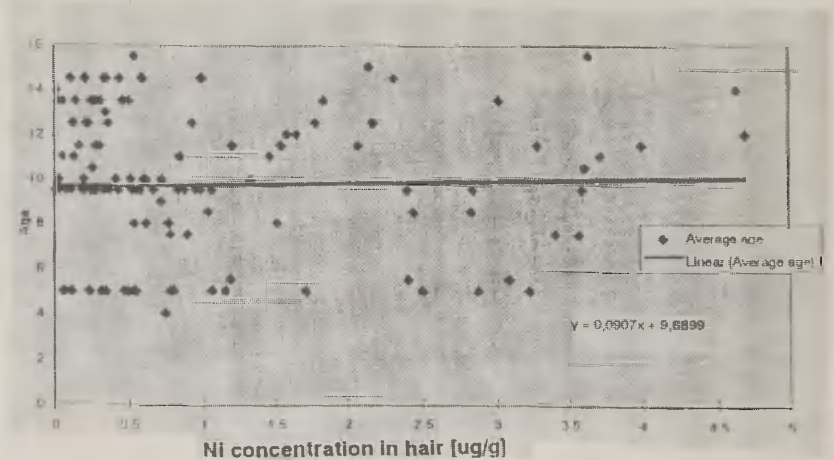


Figure 2. Ni concentration in hair in relation to age.

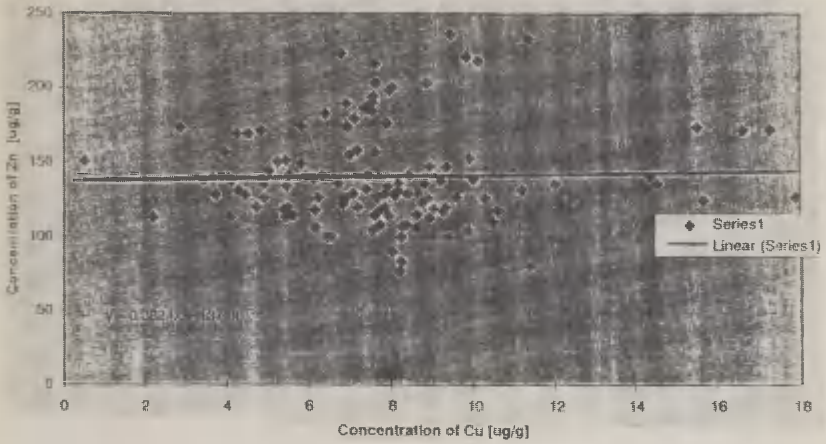


Figure 3. Correlation between Cu and Zn in hair.

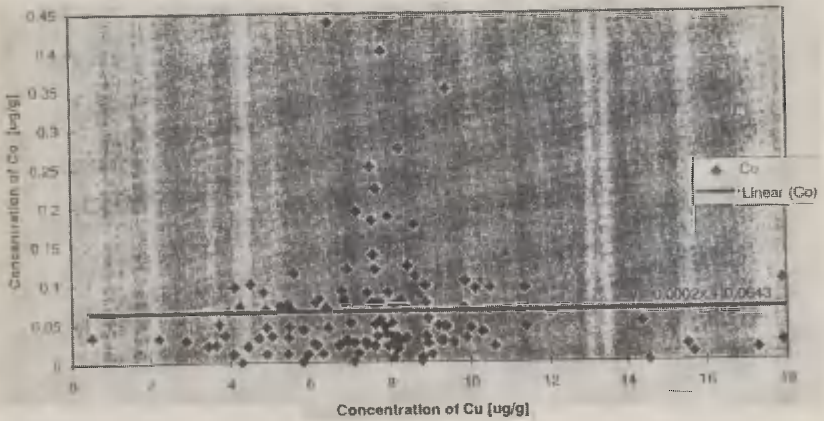


Figure 4. Correlation between Co and Cu in hair.

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THE CELPOX-BIOREACTOR

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The industrial aerobic biochemical process has during the last decade undergone a significant development in speeding up the reactions and improving of the efficiency of used reactors. The question is why the very similar activated sludge process has not at all followed the development or gained anything by the improvements. Both processes mainly require a quick solution of oxygen in the water and an equally quick simultaneous transfer of the dissolved molecular oxygen into the inner of the microorganisms.

The today known aeration systems, used in activated sludge basins, can dissolve in water more or less efficiently and quickly, but none of them has the ability to rapidly transfer dissolved oxygen into the inner of the cells. The great importance of the last phase - for the process in its entity - has not been devoted any major efforts by the aerator manufactures. Their main concern has been to prove good performance figures in clean water testing.

A comprehensive study of the most popular aeration systems in Sweden and in Germany was carried out before determining the design of and applying for patent for the CELPOX.

As far as Sweden was concerned the investigation showed a striking uniformity. Fine pore bottom aeration by means of membrane aerators was predominant on the market, being of different makes, but rather in design and performance characteristics. They are all able to present good figures in oxygen solubility, but only in clean water. For the solubility in waste water the α -value varies in the range from 0.08 - 0.8.

The situation in Germany was different to Sweden. Fine pore systems were installed there as well, but not at all as self evidently as in Sweden. Different mechanical aerators were still installed in great number and new design were developed. Mechanical agitators were often added to fine pore aeration systems. Large chemical companies

developed compact biosystems for their own factories. Among them is the Hoechst Bio-Hoch-Reaktor, where the active sludge process is performed at high energy density and turbulence in the reactor [1]. The more critical and tough attitude in selecting aeration systems, found in Germany, may be caused by the fact that the energy cost there is approx. twice as high as the Scandinavian low-price water power. Suppliers of aerators must often give very strong guarantees for energy consumption in both the short and long run, expressed as kg BOD-reduced/kWh obtained in practical operation with waste water.

The evident trend in Germany towards higher energy density in activated sludge basins caused in our design-team the question whether small and powerless rising air bubbles were the right procedure to supply the living cell mass with oxygen and to form a base for rapid and efficient biooxidation.

In order to design a new reaction system, able to meet the sophisticated and important requirements of an actively operating biomass, the CELPOX design group was completed by microbiological and biochemical experts. It soon became obvious that dissolving oxygen in water was a far smaller problem than having the dissolved rapidly and in large enough quantities transferred into the inner of the cells, where the main elimination of dissolved pollutants and metabolism takes place.

The most important and also very critical cooperation partner of any aeration system is the microorganism, which has the ability to reduce, within its cell wall, the content of dissolved organic materials in the water in the activated sludge basin. The bacteria cell is principally built as per Figure 1.

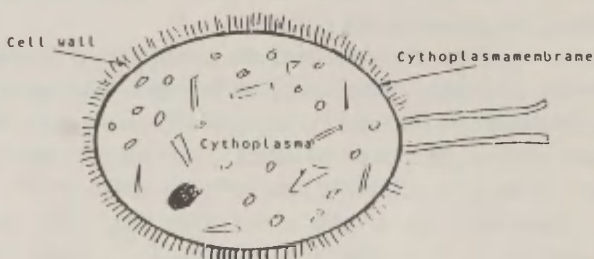


Figure 1. The bacteria cell.

The size of the cell is approx. 1/1000 of a millimetre. The cell wall is elastic and permits penetration of salts and low molecular substances in both directions. It principally fulfils mechanical functions. The cytoplasmic membrane is semipermeable and controls the in- and outlet of dissolved substances and osmotic pressure in the cell. Cytoplasm is a colloidal suspension containing hydrocarbonates, proteins, bacterial nucleus carrying the DNA and for the protein synthesis necessary ribonucleic acid, RNA.

The main part of the biochemical oxidation and metabolism takes place within the cell. Therefore all materials taking part in the processes such as carbon sources and molecular oxygen have to be transported into the cell. In order to achieve an optimum of metabolism, the concentration of the nutritive salts and metabolites has to be kept in quite narrow limits. The solution of oxygen in the water as well as the selective transfer of metabolites through the cytoplasmic membrane are diffusion mechanisms. The diffusion speed of the oxygen molecules through the membrane is entirely depending on the difference between oxygen content inside and outside of the cell. It is easily realised that a high content of dissolved molecular oxygen in the waste water outside the cell rapidly forces the oxygen into the cell. A constantly high oxygen content in the closest surroundings of each cell can only be maintained by a strong turbulence in the water. Strong turbulence can on the other hand only be maintained by having a high energy density in the water mass.

Quick and effective water purification processes by means of aerobic organisms can easily be found in nature. Since the glacial period, every waterfall or rapid, even a small one, is an effective bioreactor where the biooxidation process never will suffer under oxygen limitation. In its wisdom nature has given every falling water jet the ability to draw large volumes of air through the underlying water surface. In the turbulence and high energy density, concentrated to the impact area under every falling water jet, all necessary conditions and provisions for a rapid diffusion through the biological membranes are fulfilled. Big differences in concentration of oxygen and metabolites on the both side of the membranes are maintained. The floc structure of the organisms is disintegrated. Oxygen and substrate can quickly and easily penetrate through the vast free surface of the biomass.

Calculation and dimensioning of modern industrial bioreactors, incorporating gas/liquor mass transfer as a crucial step of the process,

are today carried out under respectful attention to the influence of convective diffusion caused by turbulence and shear forces in the liquor, as stated by Brauer [2]. The influence of convective diffusion in the mass transfer is to be compared to increased convective cold transfer in windy days, experienced by everyone of us. The significance of shear forces in the activated sludge process is well documented by Pasveer [3], declaring and proving that the speed and efficiency of the biochemical process depends on the following four velocities:

1. Solution of the oxygen in the water
2. Transfer of the dissolved oxygen to the cell surface
3. Diffusion of the dissolved oxygen through the cell membrane
4. Biochemical binding of the oxygen within the cell

With respect to the energy density in the reactor the difference is astonishing between the industrial biotechnology and the active sludge process. The industry has continuously increased the energy input in its processes and today there are bioreactors with up to 25000 watt/m³. A conventional active sludge process holds today, as it did some 30 years ago, approx. 20 watt/m³ [4].

It should become absurdly expensive to charge the big water volume of an activated sludge basin with a reasonably efficient turbulence and energy density. We are therefore chosen to design the CELPOX as a flow-through reactor, operating in accordance with principals found in nature.

The CELPOX is shown in Figure 2. The main-flow pump (1) is running continuously, giving a constant flow through the reactor tube (2). The jet pump (3) lifts water up into the head box (4) and delivers an intermittent or variable flow, regulated in accordance with the momentaneous BOD load in the basin. A number of powerful vertical jets are formed when the water dumps down through a number of large holes in the bottom of the head box. The jets draw considerable volumes of air down under the water level. The mixture of air and water flows downward through the reactor tube where the oxygen saturation of the participating microorganisms and surrounding water takes place. The air-water mixture is realised near the bottom of the basin where the large outflow keeps the basin floor from sediment.

Through the CELPOX reactor tube is pumped a flow of 10 - 120 m³/minute, depending on the CELPOX size. In the reactor tube the flow is extremely turbulent with an energy density of appr. 1500 watt/m³, disintegrating the air and the biomass to a fine emulsion, exposing an

overall maximal contact area for mass transfer. The content of dissolved oxygen in the reactor tube is always between 50 - 85 % of the possible saturation level. The lower oxygen level is found at very high BOD loads when the oxygen deficit is high. It is a physical impossibility to decrease the oxygen level to zero within the reactor tube, irrespective of the BOD content in the water. Consequently the biochemical oxidation speed never suffers under oxygen limitation in the CELPOX reactor tube, which is often the case in conventional aeration at higher loads.

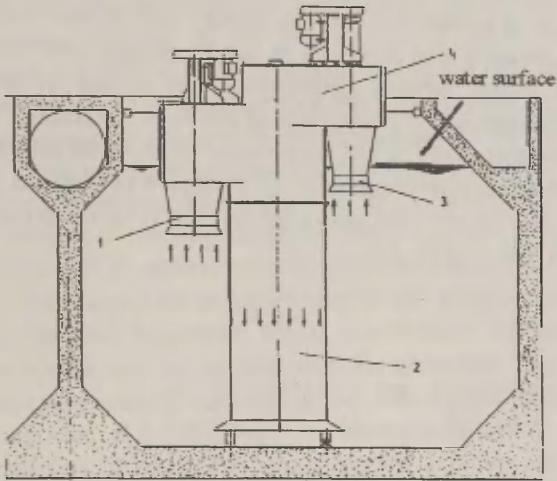


Figure 2. The CELPOX.

When the microorganisms, saturated with oxygen, leave the reactor tube for the surrounding basin water, which holds a much lower oxygen level compared to that within the reactor tube, they are forced to level out the disbalance in the concentration of the molecular oxygen inside vs. outside of the membrane. As the membrane is semipermeable, oxygen can not be ejected and the most likely way for restoring of the equilibrium is a rapid uptake of oxygen consuming or storing substances. Long before the oxygen level inside is balanced out, the microorganisms have most likely made a new trip through the CELPOX reaction tube and again been cheered up by a renewed injection of

oxygen and consecutive disbalance. In normally dimensioned CELPOX installations the microorganisms have to execute a certain number of these stressing cycles before they proceed to the following settling basin. It is well known fact that microorganisms, passing surroundings with alternately low and high concentrations of dissolved oxygen, are stressed to remarkable biochemical activities in order to level out the resulting disbalance in internal energy. The CELPOX process makes use of this peculiar feature of microorganisms, resulting in a metabolism velocity superior to any other bioreaction system.

The difference in operational characteristics is very obvious when CELPOX is compared to fine pore aeration. The contradistinction is essential as to turbulence, energy density and to the ability to disintegrate the biomass floc structure in the oxydation zone. The bigger the flocs, the higher oxygen concentration is needed in order to avoid oxygen shortage in the inner parts of the flocs. According to an investigation of Wuhrmann [5], the whole water mass in an active sludge basin must keep considerable amounts of dissolved oxygen, as a function of floc size, if 0.01 mg/litre dissolved oxygen is to be found in the inner part of the floc (Figure 3.).

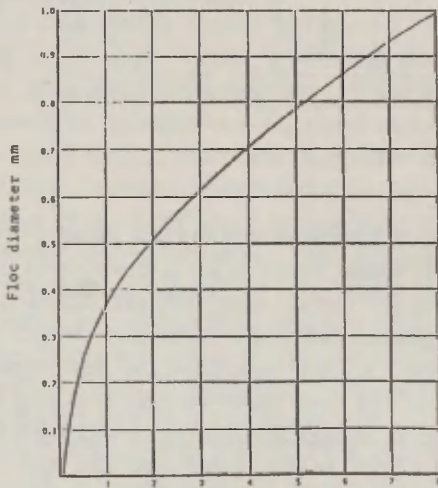


Figure 3. Dissolved oxygen in basin mg/liter.

In fine pore aeration systems there is an apparent risk that the inner parts of the flocs will suffer under oxygen limitation when the concentration of incoming dissolved substances is so high that the outer parts of the floc consumes all the available oxygen. If that is the case the speed of the biodegradation will become limited until the load decreases again. Proof for this statement will be found in the fact that the fine pore aeration is subject to very big variation in the α -value, depending on the incoming load of oxygen demanding substances.

The biomass in a CELPOX plant is subject to continuous changes between an intense aerobic state in the reactor tube and a comparatively calm state outside the reactor tube with a significantly lower oxygen level. Besides the rapid biooxidation process an extensive adsorption of dissolved organic material to the biomass takes place. During the passage through the CELPOX tube the structure of the biomass particles will be disintegrated to very small suspended flocs containing only a few bacteria. Consequently the area of biomass, exposed for adsorption, is up to 100 times larger in the circulation flow just leaving the CELPOX tube outside in the calm surrounding basin. Due to the altered concentration of dissolved oxygen in the loop of the CELPOX process, a considerable biological removal of phosphorus can be achieved, (Barnard, [6]).

A clean bottom and no sedimentation in the aeration basin was in old times considered important for a trouble-free activated sludge process. The reason was an obvious risk for anaerobic degradation of settled organic compounds, producing poisonous hydrogen sulphide. Hydrogen sulphide, H_2S , dissolved in water is harmful for microorganisms and can cause periodical stagnation of biooxidation. In all CELPOX plants the large circulation flow is directed along the basin bottom keeping it clean and free from sediment.

In practical full scale operation in industrial and municipal treatment plants, CELPOX has proved an energy efficiency in the range of 1.5 - 3.5 kg BOD-reduced/kWh, not deteriorating in course of years. According to a survey made by the International Energy Agency of OECD [7], mechanical surface aerators eliminate 0.7 kg BOD/kWh and submerged turbine aerators 0.8. New fine pore bottom aerators can be as effective as 1.1 kg BOD/kWh, but only as long as they still are clean and flexible. All OECD figures represent the high end of results for every investigated class.

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CATALYSIS DURING ELECTROLYTIC REDUCTION ON Hg-DROPPING ELECTRODE OF Co(II) COMPLEXES WITH HISTAMINE

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Single stepped electrolytic reduction on Hg-dropping electrode of mono-bi-tri-ligand complexes of Co(II) with histamine is accompanied by catalytic production of hydrogen.

Tetraligand and aquacomplexes do not display this property. The rate constants of protonation (recombination) of histamine in catalytically active mono-bi-tri-ligand complexes of O-valence Co have been calculated. Which are consequently equal to $2.0 \cdot 10^4$, $2.1 \cdot 10^4$, $3.2 \cdot 10^4$ mole⁻¹·s. The formation constant for tri- and tetra legend complexes is consequently equal to $5.6 \cdot 10^4$ and $3.7 \cdot 10^4$ l·mole⁻¹.

UMWELTVERSCHMUTZUNG, BEWAHRUNG DER KULTURDENKMÄLER UND RESTAURIERUNGS- PROBLEME AUF DEM BEISPIEL DER ST. JOHANNISKIRCHE IN TARTU/DORPAT

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Probleme der Bewahrung der Kulturdenkmäler, die sich aus der zunehmenden Umweltverschmutzung ergeben, sind besonders in Europa, darunter auch in Estland sehr aktuell geworden. Während der letzten Jahrzehnte hat man darauf immer mehr Aufmerksamkeit gewidmet. Wir müssen imstande sein, sowohl die umgebende Natur, unsere Lebensumwelt als auch unsere Kulturdenkmäler lebendig zu bewahren. Probleme der Bewahrung und Restaurierung der Kulturdenkmäler wurden besonders aktuell wegen der Zerstörungen im II. Weltkrieg. Die Hauptgefahr für die Lebensumwelt und Kulturdenkmäler ist mit riesigem Fortschritt in der Industrie, im Transport und Verkehr verbunden. Das alles hat eine kolossale Verschmutzung mit sich gebracht - die Verschmutzung der Luft, des Wassers und der Erde [1].

Vom Gesichtspunkt des vorliegenden Themas aus ist besonders gefährlich die Luftverschmutzung, da alle schon geschaffte und auch zukünftige materielle und auf Materialien bewahrende Kulturdenkmäler sich in diesem Umwelt befinden. Weder anorganische noch organische Materialien sind vor der Wirkung der in der Luft enthaltenen aggressiven (hauptsächlich säurehaltigen) Verschmutzungskomponenten geschützt [2, 3, 4].

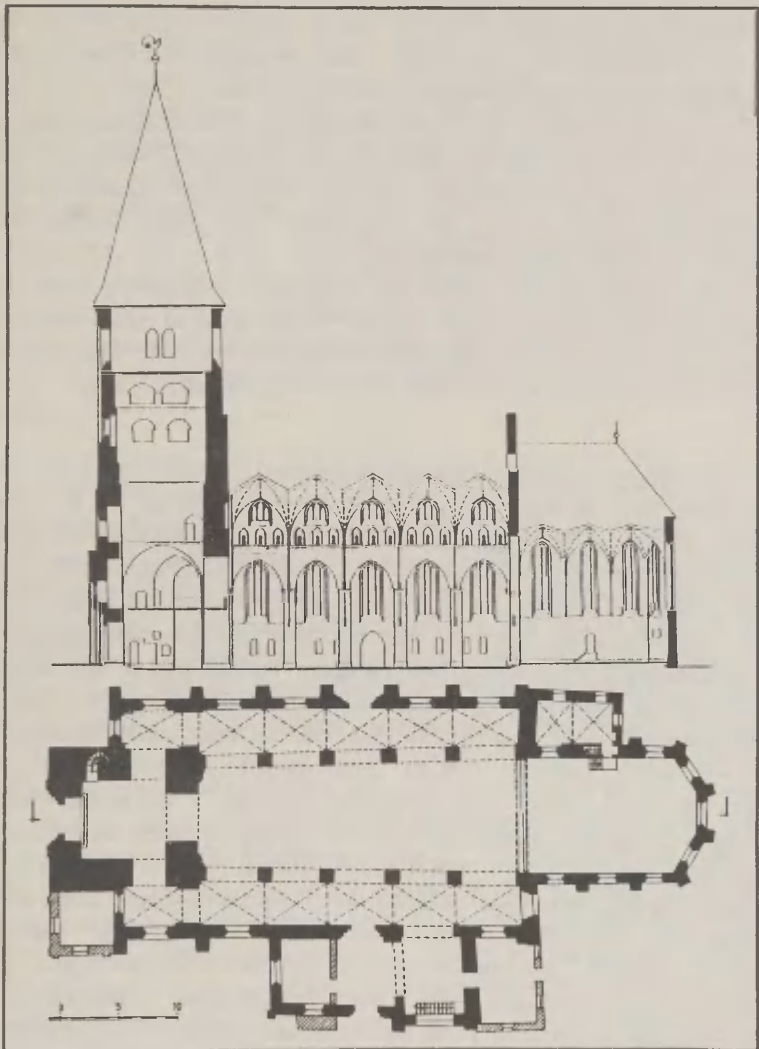
Mit der Bewahrung der Kulturdenkmäler und Restaurierungsproblemen beschäftigt sich in der UN UNESCO. Man hat verschiedene internationale Organisationen gegründet (ICCROM, ICOMOS, EURO CARE u. a.), man organisiert wissenschaftliche Symposien, Konferenzen, Sommerakademien, man realisiert betreffende Projekte, man führt unterschiedliche Ausbildungen auf dem Gebiete der Restaurierung durch usw. [5].

Eine wichtige Stelle im zahlreichen Themenbereich haben die ausführliche Erforschung der chemischen und physikalischen Prozesse zwischen Luftverschmutzungskomponenten und Materialien, die für die Schaffung der Kulturdenkmäler benutzt worden sind, die Charakterisierung der Reaktionsprodukte, das Herausfinden der quantitativen Beziehungen. Ebenfalls die Entfernung der Zerfallsprodukte und das Stoppen der weiteren Zerstörung der Materialien (Konservierung) und die Ausarbeitung der brauchbaren Restaurierungsmethodiken. Bewahrung und Beschützung der Kulturdenkmäler fordert eine enge Zusammenarbeit zwischen sehr vielen Fachspezialisten. Das ist eine interdisziplinäre Tätigkeit, wo jeder Spezialist sein wesentliches Wort zu sagen hat, um einen Arbeitsplan, der mit heutigen Anforderungen und internationalen Vereinbarungen im Einklang steht, auszuarbeiten.

Es gibt in Estland viele historisch und kulturhistorisch wertvolle Baudenkmäler - darunter auch Sakralbauten - die in einem sehr schlechten Zustand oder vom Verfall bedroht sind. Ihre Restaurierung fordert gründliche naturwissenschaftliche Voruntersuchungen, bei denen chemische und physikalisch-chemische Methoden eine besondere Rolle spielen.

Eines der einzigartigsten architektonischen und historischen Denkmäler in Nordeuropa ist die aus dem XII. - XIV. Jahrhundert stammende St. Johanniskirche zu Tartu (Dorpat), Backsteinbau aus glasierten und nichtglasierten Ziegelsteinen mit reichhaltigen Terrakottafiguren und Terrakottaschmuck. Während der Kriegshandlungen im August 1944 wurde die Kirche nahezu zerstört. Nachdem die Kirche 50 Jahre lang in Ruinen gestanden hat, sind heute die Bauarbeiten für die Restaurierung in vollem Gang, um erhaltene Teile zu restaurieren und fehlende Teile zu renovieren. Das heißt - um die Kirche in ihrem ehemaligen Gestalt neu aufzubauen.

Die St. Johanniskirche in Tartu - Dorpat ist eine der ältesten, wenn nicht die älteste von Sakralbauten in Estland und ein bedeutendes mittelalterliches historisches und Architekturdenkmal. Nach der Meinung des ehemaligen Professors für Kunstgeschichte der Universität Tartu - Voldemar Vaga - ist die Kirche ohne Zweifel ein einmaliger Vertreter der mittelalterlichen Ziegelgotik in ganz Nordeuropa. Die Aufmerksamkeit muß man auf ihre Architektur, noch mehr aber auf die zahlreichen Terrakotta richten' [6]. Kaur Altoa, Lektor für Kunstgeschichte an der Universität Tartu, behauptet daß in der gesamten



St. Johanniskirche in Tartu/Dorpat [7].

europäischen Gotik es kein anderes Bauwerk gibt, das mit der St. Johanniskirche in der Zahl der entsprechenden Plastiken, ihren Ausmaßen und ihrer künstlerischen Ausführung auch nur annähernd vergleichen werden könnte. Darin überragt die Kirche in Tartu/Dorpat/ alle Beispiele in der gesamten Gotik [7]. Die St. Johanniskirche ist auch eng mit der Geschichte der Universität Tartu verbunden. In dieser Kirche hat die feierliche Einweihungszeremonie der im Jahre 1632 vom schwedischen König Gustav II Adolf gegründeten Universität Academia Gustaviana stattgefunden. Ebenso haben bei den Wiedereröffnungen - 1690, der Academia Gustavo Carolina - und 1802 Eröffnungs - Feierlichkeiten stattgefunden. 1802 nahm die Universität ihre Arbeit wieder auf, ununterbrochen bis heute gedauert hat [8].

Die Geschichte der Kirche ist lang und kompliziert. Nach den archeologischen Ausgrabungen in der Kirche und in ihrer nächsten Umgebung wird vermutet, daß ihre Geschichte bis zum Ende des 12. oder bis zum Anfang des 13. Jahrhunderts zurückreicht [9, 10].

Mit den architektonischen und baulichen Untersuchungen hat man sich mehr oder weniger seit der 60er Jahre beschäftigt. In den 80er Jahren wurde gründlicher mit den Vorbereitungsarbeiten für den Wiederaufbau der Kirche begonnen. 1986 entwickelte Architekt K. Aluve ein Wiederaufbauprojekt für die Kirche als Konzertsaal. Endlich war es so weit, daß 1989 polnische Restauratoren mit Befestigungsarbeiten des Fundaments begannen. Ihre Tätigkeit endete wegen der Veränderung der politischen Lage im Baltikum und in Polen. 1991 wurde beschlossen, die Kirche in der Funktion einer Kirche wiederaufzubauen und möglichst genau so wie in ihrer mittelalterlichen Gestalt. Im November 1991, nach dem Weggang von PKZ, setzte die Firma "Wunibald" der Evangelisch-Lutherischen Kirche Estlands die Arbeiten fort und daraus entwickelte sich später die Firma "Stinger". Diese Firma ist bis heute bei dem Wiederaufbau der St. Johanniskirche tätig. Dem Beginn der Arbeiten der polnischen Firma PKZ gingen während mehrerer Jahren gründliche archäologische Ausgrabungen und architektonische, bauliche und kunstgeschichtliche Untersuchungen voraus [9]. 1992 wurde in Tartu zur Unterstützung der Wiederaufbau - und Restaurierungsarbeiten eine Stiftung der St. Johanniskirche gegründet.

Folgendermaßen werden wir näher Probleme, die bei der Restaurierung der St. Johanniskirche mit chemischen, physikochemischen und physikalischen Voruntersuchungen verbunden sind, betrachten. Wir versuchen es aufzuklären, welche Mängel bisher in diesem Bereich schon aufgetreten sind. Woran man schon heute arbeitet und was noch unbedingt zu tun ist, um die Kirche auf Grund der international anerkannten Grundsätzen zu restaurieren.

Der Zustand der Kirche ist in den letzten Jahren beträchtlich schlechter geworden, aufgrund der verstärkten Verfallprozesse des Ziegelmaterials und Terrakottafiguren durch die Witterung und das Einsinken der Fundamente. Auf die Ziegelwände und besonders auf die Terrakotten hat die große Luftverschmutzung des Stadtzentrums stark gewirkt, die bisher wegen der Steinkohlenheizung (SO_2) der Häuser sehr stark war. Auch der Autoverkehr ist im Stadtzentrum verhältnismäßig dicht und leistet seinen Anteil an der Luftverschmutzung (NO_x). Auch Wasser und Eis haben auf dachlose Mauernteile zersetzend gewirkt.

Um dem weiteren Verfall des Terrakottaschmucks der St. Johanniskirche zu Dorpat Einhalt zu gebieten, ihn zu reinigen, zu konservieren, zu restaurieren und neue Schmuckelemente herzustellen, müssen zunächst verschieden chemische, physikalisch-chemische und physikalische Untersuchungen durchgeführt werden. Wie die in Tartu und Stuttgart durchgeführten Vorarbeiten gezeigt haben, werden die Schäden und der Verfall der Terrakottafiguren und anderer Teile der Backsteinkirche vor allem durch atmosphärische Schadstoffe (SO_2 , NO_x , Cl^- usw.) hervorgerufen. An unterschiedlichen Teilen der Kirche ist die Zusammensetzung der den Verfall bedingenden Salze verschieden. Daher ist eine genaue Feststellung der Zusammensetzung der Schadstoffe und des Umfangs der Schäden notwendig. Nur auf dieser Grundlage ist die Wahl der Reinigungs- und Restaurierungsmethoden möglich. In einigen Fällen sind Schäden vermutlich auf lithotrophe Mikroorganismen zurückzuführen. Als Beweis könnte die äußerst intensive Entstehung von Nitraten gelten. Offensichtlich ist eine befriedigende Lösung des Problems der Zusammensetzung der Schadstoffe aber nur unter Verwendung von modernsten Untersuchungsmethoden möglich.

Die Widerstandskraft der Terrakottaelemente den Umwelteinflüssen gegenüber ist sehr verschieden, das gleiche gilt auch für Backsteine. Einige haben unter gleichen Bedingungen Jahrhunderte überdauert -

500 bis 600 Jahre, andere dagegen nicht. Daher ergibt sich das Hauptproblem: mit Hilfe der modernsten Untersuchungsmethoden festzustellen, wo die Gründe für diese Unterschiede liegen. Besonders wichtig ist das im Hinblick auf: das Ersetzen der beschädigten Terrakottazier durch die neue, vor allem an der Außenfassade der Kirche. Offensichtlich hat man zur Herstellung aller Terrakottafiguren und Backsteine, die bei der Kirche eingesetzt wurden, Lehm aus der Nähe von Tartu verwendet. Bis jetzt weiß man jedoch nicht, ob zur Herstellung von Terrakottaschmuck Devon- oder Quarternar-Lehme verwendet wurden. Man braucht eine größere Menge Terrakottafiguren, um das zerstörte Nordschiff und andere Teile der Kirche wieder aufzubauen, vermutlich über 100. Aus diesem Grunde müssen Lehmfundstellen wiedergefunden werden, wo man Lehm zur Herstellung der widerstandsfähigeren Figuren gewonnen hat. Ein Problem für sich ist auch das Anhalten des Verfalls der beschädigten Terrakottafiguren. Dazu müssen verschiedene Konservierungsmittel verwendet werden. Bis jetzt ist noch nicht klar, welcher Steinfestiger am besten geeignet ist. Dazu sind umfangreiche Forschungsarbeiten nötig. Ein Kapitel für sich sind Putze und Mörtel. Die bisherige Forschung hat gezeigt, daß ihre Zusammensetzung durch Jahrhunderte verschieden und charakteristisch für unterschiedliche Bauperioden ist.

Die Ergebnisse der chemischen und physikalisch-chemischen Untersuchung der St. Johanniskirche können auch bei der Vorbereitung der Restaurierung anderer estnischer Denkmäler der Backsteinarchitektur verwendet werden. Leider befinden sich solche Arbeiten an der St. Johanniskirche erst im Anfangsstadium, bisher hat man wenig Wesentliches geleistet.

Die bisherigen Arbeiten, die an der Kirche gemacht wurden, sind rein mit baulichen Problemen verbunden gewesen - Bau der Abstützungssysteme, Befestigung der Fundamente, Aufstellung der Zwischenboden des Turmes u. a. Die Durchführung der Befestigungsarbeiten der Kirche ist sehr kostspielig und verlangt viel Geld. Deswegen ist die Firma, die Arbeit durchführt, interessiert, daß ihnen die vom Staat gegebene Summe maximal zur Verfügung steht. Auf der anderen Seite müssen bei einem Objekt wie die St. Johanniskirche parallel zu diesen Arbeiten mehrere archäologische und architekturarchäologische Untersuchungen durchgeführt werden. Diese Untersuchungen brauchen ebenso Geld, und die kann man nicht unbeendet

lassen. Dazu verpflichtet ein jetzt in Estland im März 1994 eingebrachtes Gesetz zum Denkmalschutz. Übrigens kommt es öfter vor, daß bei uns in Estland auf die naturwissenschaftliche Voruntersuchungen nicht nötige Aufmerksamkeit gerichtet wird. Daß das Zerstören des alten und das Errichten von etwas Neuem an dieser Stelle als Restaurieren bezeichnet wird - ist auch nicht selten. Das Denkmalschutzgesetz mußte auch hier Ordnung schaffen. Einige Baufirmen, die sich klangvoll als Restauratoren bezeichnen, haben oft keine Ahnung, was heute unter Konservieren und Restaurieren zu verstehen ist. Meistens fehlt für solche Arbeit die Sondervorbereitung auf dem nötigen Niveau. Das Hauptziel ist Geshäfte zu machen. Mit den Fragen zu dem Restaurieren der wichtigen Objekte hat man sich oft an ausländische Spezialisten gewandt. Man hat mit erfahrenen ausländischen Firmen zusammengearbeitet wie jetzt an der St. Johanniskirche - die Befestigungsarbeiten werden zusammen mit einer finnischen Firma durchgeführt.

Die St. Johanniskirche ist unikal Bau. Unikal ist alles das, was mit ihr geschehen ist und was geschieht. Unikal ist das Material, voraus sie gemacht ist, unikal ist das Klima in dem sie sich befindet, die Verschmutzung und die Prozesse, die mit ihr geschehen. Es fehlt uns analoges Vergleichsmaterial, wir können hier keine Säuberungs-, Konservierungs-, Restaurierungsmethoden benutzen, bevor keine nötige Analysen gemacht worden sind, Ausarbeitung von passenden Säuberungs-, Konservierungs-, Restaurierungsmethoden oder genaues Überprüfen von anders wo benutzen Methoden. Es ist höchst naiv zu meinen, daß irgendwo fertige Rezepte schon vorhanden sind, die man auf Schritt und Tritt benutzen kann. Das alles nimmt Zeit, schöpferische Arbeit und natürlich auch Geld in Anspruch. Diese Arbeit kann man nicht mehr in die Länge ziehen, wie man das bisher gemacht hat.

Die St. Johanniskirche ist vom Standpunkt der Untersuchung der Geschichte der technologischen Seite des Bauwesen ein sehr wichtiges Objekt in Estland. Hierher bekommen wir entsprechende Informationen aus jahrhundertelanger Zeitperiode, über die Materialien, die in verschiedenen Bauetappen benutzt worden sind, über ihren Bestand, ihre Eigenschaften, Anfertigung u. a. Besonders wichtig ist für die folgenden Untersuchungen aus diesen Teilen der Kirche Proben zu nehmen, die während der Wiederaufbauarbeiten zerstört werden.

Wesentliche Problemen tauchen mit dem Beginn des Wiederaufbaus der zerstörten Teile der Kirche auf. Architekt Udo Tiirmaa, der die bauliche Seite der Kirche gründlich untersucht hat, gibt in seinem

Artikel einen Überblick über die glasurbedeckten und nicht glasurbedeckten Profilziegel [11]. Die Zahl von Varianten ist sehr groß und von der Gestaltung her vielseitig. Außerdem ist die Zahl von speziellen Ziegeln mit verschiedenen Maßen sehr groß. Die kann man nicht industriell herstellen, sondern handwerklich. Hierher muß man auch das Anfertigen von zahlreichen großmaßstäblichen Terrakotten zählen, von denen jede ein Kunstwerk darstellen muß. Dafür ist es notwendig, einen eigenen kleinen Produktionsbetrieb zu gründen. Die polnischen Restauratoren begannen bei Tartu, auf einem Platz der alten Ziegelindustrie, mit der Gründung einer solchen Keramik die für den Wiederaufbau der Kirche notwendig ist. Das aber blieb unvollendet und ist jetzt nicht mehr vorangeschritten. Es wird nur gestritten - aber die Ernsthaftigkeit des Problems ist geblieben und bisher hat man keine passende Lösung gefunden. Für die Durchführung von Mauerarbeiten braucht man Ziegel und Kalkmörtel aus guter Qualität. Mit Ziegeln aus nicht guter Qualität und Zementmörtel kann man bei einem solchen Bau nichts machen. In dieser Hinsicht haben wir sowohl in Estland als auch anderswo ausreichend schlechte Erfahrungen gemacht. Es ist Zeit, auch darauf zu achten.

Vom Obenerwähnten ausgehend sollten die Untersuchungen folgende Gebiete umfassen.

1. Ermittlung der chemischen und mineralischen Zusammensetzung der Untersuchungsobjekte. Genaue Analysen - auch der Spurelemente - ermöglichen eine ausführliche Beschreibung und Zuordnung unserer mittelalterlicher keramischer Bau- und Schmuckmaterialien, die Jahrhunderten getrotzt haben. Auf der Grundlage dieser Analysen wird es möglich sein, die Fundstellen der beim Bau verwendeten Materialien (hauptsächlich Lehm und Kalkstein) in der Nähe Tartu wiederzufinden. Aus Lehm gleicher Zusammensetzung können die für die Restaurierung der Kirche benötigten fehlenden architektonischen Details und Backsteine hergestellt werden. Durch neuere physikalische Untersuchungsmethoden kann auch das Alter der Keramik ermittelt werden, die sich nicht in der Brandzone befand. Besonders notwendig ist die Ermittlung der Zusammensetzung der alten Glasuren - Analyse und Ausarbeitung von geeigneten Analyseverfahren. Zu dieser Etappe gehört auch Analyse und Testen zur Herstellung der fehlenden keramischen Details benötigten Lehms.

2. Ermittlung des Charakters und Ausmaßes der durch die Umwelteinflüsse verursachten Schäden. Hierbei müssen zweierlei Untersuchungen durchgeführt werden. Erstens ist Zusammensetzung und Gefährdungspotential der Oberflächenverschmutzung festzustellen, wodurch eine bewußte Entscheidung zugunsten einer bestimmten Methode zu ihrer Beseitigung möglich wird. Zweitens müssen Zusammensetzung und Menge der Salze, die aus dem Inneren der Objekte und durch Immissionen an die Oberfläche treten, ermittelt werden, um die Ursachen dieses Prozesses festzustellen und geeignete Behandlungsmethoden zu finden.

3. Ausarbeitung der zur Beseitigung der Schäden geeigneten Methodik (Restaurierungstechniken). Sie setzt den Zugang zur Information über Terrakottakeramik in den internationalen Datenbanken zu Fragen der Restaurierung der Baudenkmäler sowie Durcharbeiten der einschlägigen Literatur und Kennenlernen der praktischen Erfahrung und der angewendeten Technologien voraus.

4. Ermittlung der Zusammensetzung der zur Befestigung der Terrakottadetails und Ziegel verwendeten historischen Bindemittel (Putz, Mörtel, Stuck, Anstrich, Kleber) durch quantitative chemische Analyse und Strukturanalyse. Die Erforschung der im Mittelalter in den verschiedenen Bauebenen und während der Reparaturen der Kirche verwendeten Bindemittel und chronologische Unterscheidung der verschiedenen Bauperioden. Die Ermittlung der Zusammensetzung der Putze und Mörtel gestatten es, sie zu reproduzieren und bei der Restaurierung zu verwenden.

5. Ausarbeitung der für estnische Bedingungen geeigneten Methoden zum Reinigen, zur Konservierung und Restaurierung der Terrakottakeramik. Ausgehend von den Untersuchungsergebnisse, Analysen und gestützt auf international praktische Erfahrungen sollen für unsere Bedingungen geeignete Restaurierungskonzeption und -technologien ausgearbeitet werden.

Zum Zusammenstellen eines Restaurierungsprojektes auf dem heutigen Niveau ist vorerst die Restaurierungskonzeption auszuarbeiten. Das heißt, was man zusammengefaßt zu erreichen versucht und was man machen muß, um dieses Ziel zu erreichen. Bei der St. Johannis-kirche sind für Erreichem von Lösungen der aufgestellten Probleme nötig: 1) Konservieren, 2) Restaurieren und 3) Renovieren, d. h. Neuaufbau der völlig zerstörten Teile des Baus zusammen mit den zu diesen Teilen gehörenden Gegenständen (z. B. Terrakotten). Rolf Wihr

erwähnt in seinem bekannten Handbuch [12]: "Bei allen Maßnahmen hat zunächst die Konservierung, die Erhaltung und Sicherung aller alten, noch vorhandenen Substanz, im Vordergrund zu stehen. Sie ist deshalb am wichtigsten, weil oft Material erhalten werden muß, dessen Zerfall nicht aufzuhalten ist und das rettungslos verloren zu scheint". Und weiter "Ist Zweck der Konservierung die reine Erhaltung des gefährdeten Objekts mit allen dazu notwendigen Arbeitsgängen, so ist die Restaurierung erst auf der Konservierung aufbauende Maßnahme".

In der Altstadt Tartu haben wir keine Übersicht darüber, wie groß ist das Einhalten von SO_2 , NO_x und anderer Verschmutzungsstoffe in der Luft wegen immer größer werdenden Verkehrs und übrigen Luftverschmutzer. Es ist äußerst notwendig, vorläufig wenigstens in der Altstadt ständig wirkenden Luftanalysen-Punkte zu organisieren, von denen sich der eine unmittelbar in der Nähe von Johanniskirche befinden muß. Im Interesse der Einwohner der Altstadt, der Universität, vieler Behörden und Architektur - und Kunstdenkmäler ist es notwendig, ein Kontrollsystem über Luftzustand zu schaffen.

Am Institut für Organische Chemie der Universität Tartu, wo auch Chemiker-Restauratoren vobereitet werden, beteiligt sich seit 1992 auf eigene Initiative an der Lösung der mit der Restaurierung der St. Johanniskirche zu Tartu verbundenen chemischen Probleme, weil das Gebiet unerforscht und vernachlässigt war.

Am Institut wurde 1992 eine Diplomarbeit geschrieben und verteidigt, die die chemische Zusammensetzung der Glasuren der St. Johanniskirche behandelte [13].

Dank der Sponsoren und des Vereins für Estnischen Denkmalschutz konnte man am Ende des Jahres 1992 und im Frühling des Jahres 1993 dasselbe mit heutigen modernsten Methoden in Finnland an der Universität Oulu weiteruntersuchen. Ebenso hatte man die Möglichkeit (Lindy Piiri) mit Unterstützung des Nordländischen Fonds im August 1993 an der Arbeit am Konservierungsinstitut an der Universität Göteborg im Rahmen der Summer Academy mit dem Thema "Air Pollution and Conservation" teilnehmen. Äußerst wichtig war der Aufenthalt im November/Dezember 1993 in Stuttgart am Otto-Graf-Institut, der dank des Entgegenkommens des Instituts und der energischen Organisationsarbeit eines Entusiasten der Restaurierung der St. Johan-

niskirche, Herrn Hardy Engelbrecht und dank der Hilfe und Unterstützung seiner Gleichgesinnten in Deutschland, verwirklicht wurde.

An diesem kompetenten Institute konnte man sich mit heutigen neuesten Untersuchungsmethoden vertraut machen, die beim Lösen der obenwähnten Probleme gebraucht werden. Es war möglich, einen Überblick die neuere Fachliteratur zu bekommen und die Analysen der Materialproben von der St. Johanniskirche praktisch durchzuführen. Es wurden der Typ der Verschmutzung auf den Außenwänden der Kirche und die Säuberungsmöglichkeiten untersucht. Offensichtlich ist eine Modus am produktivsten, bei dem einige Analysen und Untersuchungen bei uns in Tartu durchgeführt werden und der Teil von der Arbeit, der die teure Apparatur benötigt, die wir nicht haben - wird als Zusammenarbeit im Ausland durchgeführt.

Es ist natürlich, daß man sich dabei auf die Erfahrungen von Ländern stützt, wo wissenschaftliche Untersuchungen auf dem Gebiet der Restaurierung ein hohes Niveau erreicht haben. Wir sind der Auffassung, daß sich bei Deutschland um einen geeigneten Partner handelt, wo die entsprechende wissenschaftliche Forschung eine Spitzenposition in der Welt einnimmt. Wir haben zu deutschen Institutionen auf diesem Gebiet auch schon enge Beziehungen.

Von der Leitung der Universität Tartu ist die Teilnahme des Instituts für Organische Chemie am wissenschaftlichen Forschungsprogramm "Neue Wissenschaft" mit dem Thema "Restaurierungskonzeption der St. Johanniskirche zu Tartu" für das Jahr 1994/95 bestätigt worden.

Am ausführlichsten sind von uns die glasierten Profilziegel von der ersten Bauperiode der St. Johanniskirche bis zu Beginn des 20. Jh. untersucht worden. Die Ergebnisse sind teils schon veröffentlicht, teils befinden sie sich in Druck [14-17].

In den Jahren 1994/1995 hat man mehrere chemische und physikalisch-chemische Untersuchungen der Glasuren, der Mörtel, Terakottamaterialien und das Enthaltenseins von Salzen sowohl im Institut für Organische Chemie in Tartu als auch im Otto-Graf Institut in Stuttgart und kürzer auch im Fraunhofer Institut für Silicatforschung in Würzburg durchgeführt. In Deutschland war es möglich dank der Hilfe der Carl Schirren Gesellschaft. Auf dem von der erwähnten Gesellschaft veranstalteten Seminar in Lüneburg 1994 wurde unser Vortrag über Restaurierungsprobleme der St. Johanniskirche vorgetragen [18].

Dies sind kurz die wesentlichen Probleme, von deren Lösung die architektonische, kunsthistorische and bauliche Qualität und die Stelle der Wiederaufgebauten St. Johanniskirche unter Kulturdenkmälern in Europa abhängt.

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IN MEMORIAM

RUDOLF WOODE

07.09.1925 - 29. 04.1995



Viljandis sündinud ja Tallinnas keskhariduse saanud Rudolf Woode lahkus Eestist 1942 a. Soome, kus võitles vabatahtlikuna vennasrahva vabaduse eest. 1944. a. jõudis ta koos teiste Soomepoistega haavatu-na Rootsi. Pärast lühiajalist viibimist põgenike laagris algas töömehepõli: algul kaevanduses, siis konstruktorina ja tööstusinsenerina.

Aastatel 1954-1958 õppis Rudolf Woode Göteborgis Chalmersi Tehnikaülikoolis masinaehituseinseneriks, töötades samal ajal konstruktorina paberivabrikus. Järgnes 10 aastat tööd mitmes paberitehases, algul insenerina, siis juhtivatel ametikohtadel paberitööstuse masinate müügi alal.

Rudolf Woode oli juurdleva loomuga andekas insener ja teadlane, kes 70. aastate algul hakkas tõsiselt huvituma keskkonnaprobleemidest. 1972. a. asutas ta firma AB Celpateknik ning asus realiseerima oma reoveepuhastusalaseid leiutisi - flotaatoreid Celflot, bioreaktoreid Celpox jt.

Rudolf Woodele oli kodumaa saatus väga südamelähedane ning pärast Eesti vabanemist asus ta aktiivselt ja omakasupüüdmatult appi meie veekaitseprobleemide lahendamisel, sealhulgas Ida-Virumaal. Tema leiutatud erakordselt efektiivsed bioreaktorid Celpox on võetud laialdaselt kasutusele mitmes Euroopa maas, ka Eestis (juba töötavad seadmed asuvad Viiratsis ja Põlvas, rakendamisel on need teisteski linnades).

Rudolf Woode lahkus meie hulgast ootamatult, ainult paar päeva pärast veekaitsele pühendatud ringsõitu kodumaal. Tema põrm puhkab Tallinna Metsakalmistui.

Need kodueestlased, kellel oli õnn Rudolf Woodega kokku puutuda ning ühist tööd teha, mäletavad tänuga heatahtlikku ja huumorimeelset sõpra ja kolleegi. Tal oli hämmastavalt lai huvide ring ning otsiva vaimuga inimesena püüdis ta kõikide probleemide lahendustes jõuda nende olemuseni. Meenuvad asjalikud vestlused nii Woodede kodus Ekeröl kui ka Eestimaal, kus alustatud mõttekäigud on inspireerinud mitmeid huvitavaid uurimistöid Tartu Ülikoolis. Nende huvitavate teemade algatamise eest võlgname tänu heale sõbrale ja mõttekaaslasele. Rudolf Woode tööd jätkavad tema pojad Jaan ja Erik.

Aleksander Maastik
Eesti Põllumajandusülikool

Toomas Tenno
Tartu Ülikool



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