

## **POSSIBILITIES OF MERCURY DISPERSION FROM CHLORINE-ALKALI ELECTROLYSIS**

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**Abstract.** Production of healthy food primarily requires complete control of agricultural resources in the vicinity of industrial objects which are potential pollutants. This problem is especially emphasised with pollutants, such as mercury, which accumulate in human body. One of the potential pollutants are chloral-alkali electrolysis facilities. Dispersion of mercury through evaporation or waste water from this type of industrial plant, in a case of an industrial accident or inadequate waste treatment, can have immense consequences. Waste waters that pour into nearby watercourses are not only water pollutants, but also permanently pollute surrounding land parcels through flooding. Since Tuzla canton has always been an industrial and mining center, with a current tendency for production and processing of healthy foods, it would be of interest to look into the efficiency of chlorine-alkali waste water treatment (while it was running in its full capacity) and by that achieve additional data needed for evaluation of conditions for production of healthy food. Method of flameless AAS using SnCl<sub>2</sub> and NaBH<sub>4</sub> as reductors was used for control of residual mercury in watercourse. Since waste waters contain interfering substances, their influence on attained concentrations was also determined. The validity of this method was confirmed by results obtained in other laboratories.

**Keywords:** mercury, flameless AAS, waste water, chlorine-alkali electrolyses.

### **AIMS AND BACKGROUND**

Mercury has been well known as an environmental pollutant. As early as the 1950's, it was established that emissions of the mercury to the environment could have serious effects on human health. These studies demonstrated that fish and other wildlife from various ecosystems commonly attain mercury levels of toxicological concern when directly affected by mercury-containing emissions from human-related activities. Human health concerns arise when fish and wildlife from these ecosystems are consumed by humans. The first symptoms of mercury poisoning are similar to the symptoms of nervous system diseases, thus once they appear a possible mercury poisoning should be considered.

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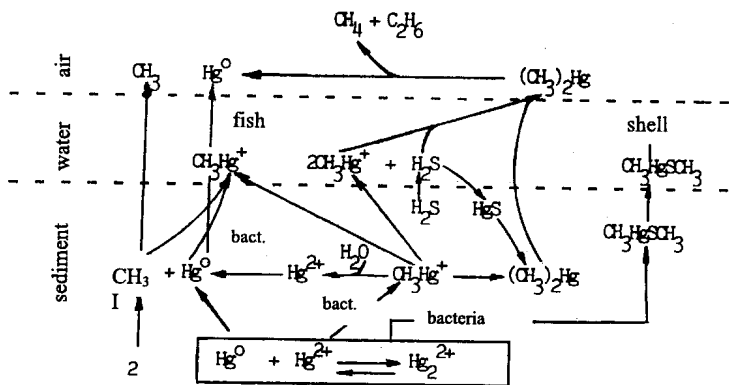


Fig. 1. Mercury cycling in nature

Up to now, research showed that, as a pollutant, mercury participates in a very complex scheme of formation of organic and inorganic compounds which are balanced among each other as it is shown in a simplified diagram in Fig. 1 (Ref. 1).

Mercury accumulates in the liver, kidney, brain and blood and can cause acute or chronic health effects. According to the standard methods for the examination of water and waste water, a maximum allowed mercury concentration (in inorganic form) in drinking and waste waters is  $0.001 \text{ mg/dm}^3$  (Ref. 2).

The Environmental Protection Agency (EPA) has set a limit of 2 parts of mercury per billion parts of drinking water (ppb). EPA currently recommends that the level of inorganic mercury in rivers, lakes and streams is to be no more than 144 parts mercury per trillion (ppt) parts of water to protect human health. EPA has determined that a daily exposure to inorganic mercury in drinking water at a level up to 2 ppb is not likely to cause any significant adverse health effects.

The Food and Drug Administration (FDA) has set a maximum permissible level of 1 part of methyl-mercury in a million parts of seafood (1 ppm).

The Occupational Safety and Health Administration (OSHA) has set limits of  $0.1 \text{ mg}$  of organic mercury per  $\text{m}^3$  of workplace air ( $0.1 \text{ mg/m}^3$ ) and  $0.05 \text{ mg/m}^3$  of metallic mercury vapour for 8-hour shifts and 40-hour workweeks<sup>3</sup>.

## FUNDAMENTALS OF CHLORINE-ALKALI ELECTROLYSIS

Production of chlorine and sodium hydroxide is based on electro-chemical process of sodium-chloride dissolution in the electrolyzers with liquid mercury as an electrode. Salty water is used as a raw material. The basic electro-chemical pro-

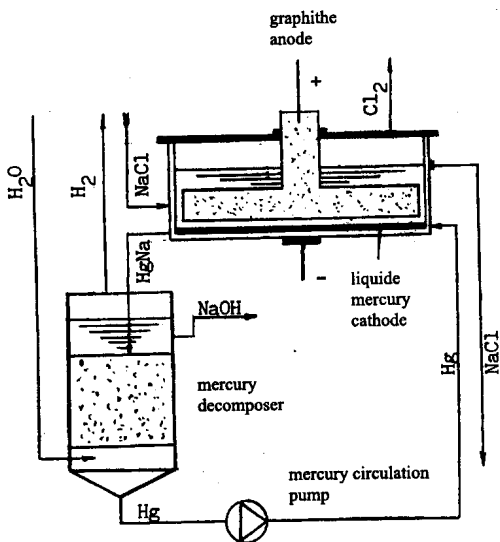
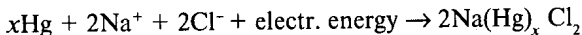
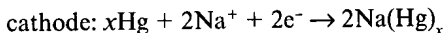
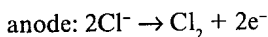
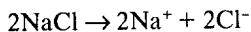


Fig. 2. Electrolysers with liquid mercury cathode

cesses are taking place in electrolysers (Fig.2) and can be represented with the following reactions:



Even though mercury leaks can be solved through a well designed construction and strict control of production, it is still possible that installation malfunction or some other accidental situation can result in mercury pollution of the environment. Figure 3 gives primary locations which can be carriers of pollution.

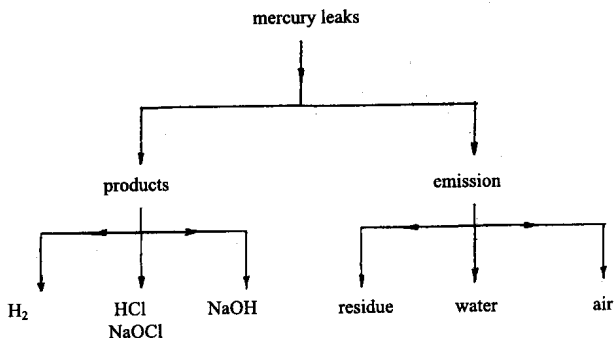


Fig. 3. Schematic representation of mercury leaks in chlorine-alkali electrolysis process

## EXPERIMENTAL

This research studied the efficiency of waste water treatment as well as control of waste water entry into watercourse at the time when this facility was running in its full capacity, thus getting an insight into a possible emission of mercury in environment.

Mercury concentrations in waste waters as well as at the watercourse entry were checked in daily analyses before and after the purification treatment, since the technological procedure is structured like that. Since waste waters collected in the facility contain a series of coexisting substance, it was necessary to determine their effect on accuracy and precision of the method for determination of mercury concentration. Due to that additional research was done at already prepared model-systems which contained coexisting substances in the concentration region as well as waste water for the treatment.

*Reagents and chemicals.* All inorganic chemicals used were of analytical reagent grade.  $\text{HgCl}_2$  (Perkin Elmer);  $\text{KMnO}_4$  (Merck);  $\text{HCl}$  (Kemika);  $\text{HNO}_3$  (Kemika);  $\text{H}_2\text{SO}_4$  (Kemika);  $\text{SnCl}_2$  (Kemika);  $\text{HONH}_2 \cdot \text{HCl}$  (Merck);  $\text{NaBH}_4$  (Kemika) and  $\text{NaOH}$  (Kemika) were used.

*Stock solutions.* Mercury stock solutions ( $1.0 \text{ mg/cm}^3$ ) were prepared by dissolving of  $\text{HgCl}_2$  in acidified water. Standard solutions of  $\text{Hg(II)}$  ( $1.0 \text{ } \mu\text{g/cm}^3$  or  $0.1 \text{ } \mu\text{g/cm}^3$ ) were diluted from the stock solution daily.

• First series is prepared from standard  $\text{HgCl}_2$  solution by dissolving it with  $\text{HNO}_3$  whose concentration was  $1 \text{ mol/dm}^3$ .

• Second series of solutions of the same  $\text{HgCl}_2$  concentration to which were added the  $\text{CaSO}_4$ ,  $\text{Mg(OH)}_2$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{NaClO}_3$  and  $\text{Ca(OH)}_2$  salts, so their ions were present in mass concentrations: chlorides  $1.042 \text{ g/dm}^3$ , sulphates  $1.902 \text{ g/dm}^3$ , chlorate  $74.51 \text{ mg/dm}^3$ , calcium  $2.05 \text{ mg/dm}^3$ ; magnesium  $0.12 \text{ mg/dm}^3$  and sodium  $1.83 \text{ g/dm}^3$ .

The samples of the waste water as well as the prepared standard solutions were acidified to pH 2 level in order to prevent any absorption of mercury into the container walls. Addition of oxidation reagents ( $\text{KMnO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$ ) prevents reduction of the ionic mercury into metal and its evaporation.  $\text{HNO}_3$  was used to acidify the samples. The samples were prepared in polyethylene bottles. The containers were carefully cleaned with  $\text{HNO}_3$  and washed with an oxidation solution.

*Methods.* Standard methods, based on determination of mercury concentration by flameless 'cold-vapour AAS', were applied in research using reductors:

a)  $\text{SnCl}_2$ , and b)  $\text{NaBH}_4$ .

*Apparatus.* The validity of this method is examined in a parallel analysis in several laboratories. Absorbance measurements of mercury were made by a

Coleman Model MAS-50 mercury analyser, Perkin Elmer ('Doo Polihem' in Tuzla and Republic Hydrometeorology Department of Serbia in Belgrad), AAS type 4000, Perkin Elmer (Republic Health Department in Sarajevo) and AAS model 373, Perkin Elmer, with an appendix for mercury finding using reduction with  $\text{NaBH}_4$ , MHS-1, Perkin Elmer (Republic Health Department in Zagreb).

## RESULTS AND DISCUSSION

The attained results are sorted according to the international standards for statistical methods for precision of the carried out research, i.e. repeatability,  $r$ , a propos reproducibility,  $R$ , of the results<sup>4</sup> and are shown on diagrams in Figs 4, 5 and 6.

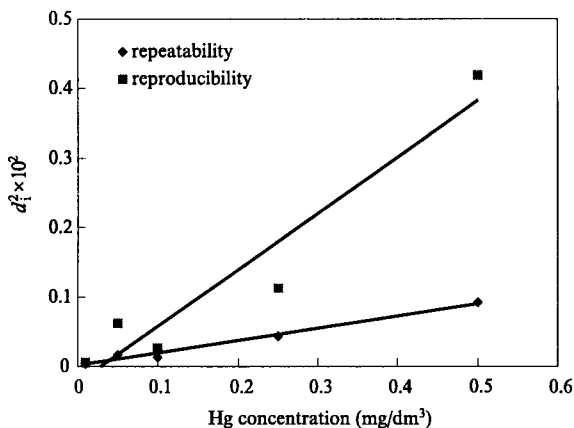


Fig. 4. Repeatability and reproducibility as a measure of precision of inter-laboratory analysis of standard mercury solutions without coexisting substances using the method of flameless AAS

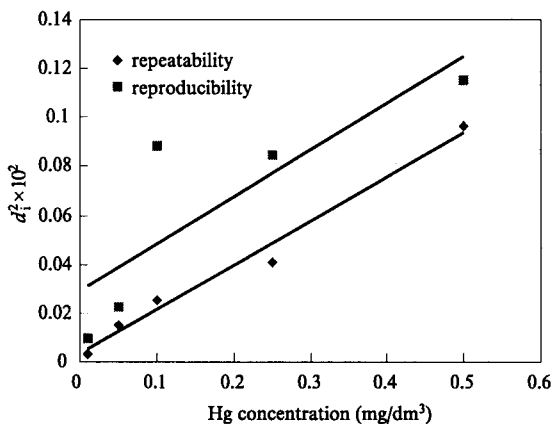
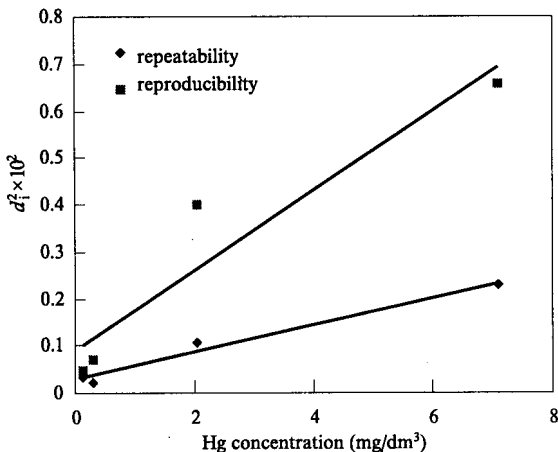


Fig. 5. Repeatability and reproducibility as a measure of precision of inter-laboratory analysis of standard mercury solutions with coexisting substances using the method of flameless AAS



**Fig. 6.** Repeatability and reproducibility as a measure of precision of inter-laboratory analysis of chlorine-alkali electrolysis waste water samples using the method of flameless AAS

The ratio  $R/r$ , i.e. the ratio of a single laboratory's and the inter-laboratories' sums of squared deviations, goes between 1.19 and 4.54.

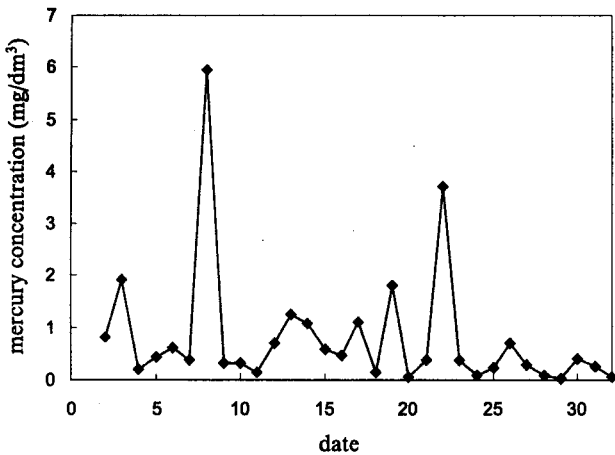
As shown on the diagrams for repeatability and reproducibility of the results using the same method and procedure, the dissipation of results around the mean value is approximately the same (coming from random error statistics) for each laboratory, and its smaller than in a case of two, three or more laboratories which arises from a systematic error due to mercury losses from solution.

Repeatability of the performed analysis is at a relatively high level in all the three laboratories regardless of the mercury concentration, composition of the sample, therefore, it can be concluded that any spectacular and other interference are not present. The results of inter-laboratory analysis of standard mercury solutions with added contaminants as well as samples of waste water show larger reproducibility than in standard mercury solutions in clear distilled water. It is assumed that samples which contain chloride ions (from NaCl) create stable bivalent mercury complexes in an acidic medium, thus preventing absorption of mercury into the container walls and, therefore, preventing mercury losses from the solutions. The difference between the attained and exact values is not significant, except for mercury solutions in pure water, without presence of chloride ions, where absorption of mercury into the container walls probably occurred.

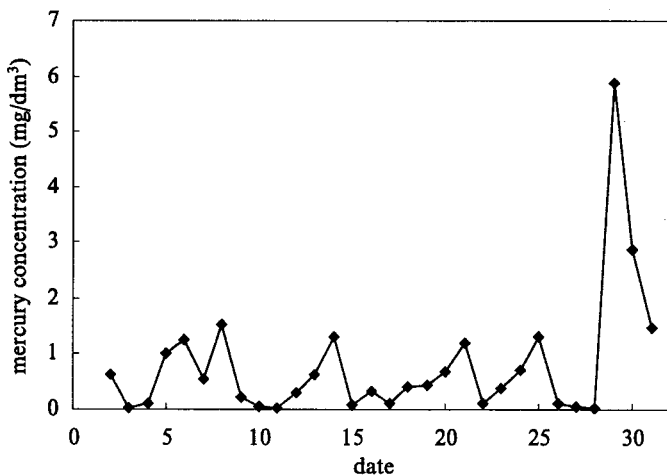
The results of the efficiency of the mercury purification and control treatments are shown in Tables 1, 2 and 3. Figures 7, 8 and 9 show the diagrams of mercury concentrations in waste waters at their entry from the chlorine-alkali facility into the watercourse.

**Table 1.** Results of study of the purification treatment efficiency and control of mercury levels in watercourse for January of 1990

Date	At the facilitie's entry		At the facilitie's exit		Purification effectivity % <i>E</i>	At the entry to the watercourse	
	water	mass	water	mass		water	mass
	volume, <i>Q</i> (m <sup>3</sup> /day)	Hg (kg/day)	volume, <i>Q</i> (kg/day)	Hg (kg/day)		volume, <i>Q</i> (m <sup>3</sup> /day)	Hg (kg/day)
1						2520	2.09
2						2540	4.9
3	120	0.732	120	0.239	67.34972678	2700	0.54
4	70	0.514	70	0.066	87.15953307	2590	1.14
5	60	0.516	60	0.026	94.96124031	2680	1.661
6						2540	0.965
7						2620	15.56
8						2600	0.83
9						2620	0.838
10	60	0.483	60	0.048	90.0621118	2590	0.414
11	60	0.432	60	0.005	98.84259259	2670	1.869
12	60	0.037	60	0.024	35.13513514	2650	3.312
13						2530	2.757
14	60	0.211	60	0.058	72.51184834	2590	1.476
15	60	0.462	60	0.006	98.7012987	2660	1.276
16						2650	2.968
17						2580	0.413
18	50	0.762	50	0.052	93.17585302	2560	4.61
19						2650	0.159
20						2600	0.988
21	60	0.819	60	0.009	98.9010989	2600	9.62
22	60	0.544	60	0.022	95.95588235	2550	0.994
23	60	0.3	60	0.06	80	2590	0.259
24	60	0.6	60	0.007	98.83333333	2640	0.633
25	60	0.825	60	0.013	98.42424242	2460	1.722
26						2420	0.677
27	60	0.057	60	0.005	91.22807018	2500	0.2
28	70	0.571	70	0.033	94.2206655	2650	0.106
29	50	0.6	50	0.06	90	2640	1.188
30	60	0.481	60	0.187	61.12266112	2590	0.647
31	60	0.489	60	0.123	74.84662577	2680	0.16
Total	1200	9.385	1200	1.063	88.67341502	80460	64.98



**Fig. 7.** Mercury concentrations in waste waters at the watercourse entry in January of 1990  
 The degree of waste waters decontamination from mercury varied between 35.14 and 98.9%. The level of mercury in purified waste water was between 0.1 and 5.94 mg/dm<sup>3</sup>



**Fig. 8.** Mercury concentrations in waste waters at the watercourse entry in June of 1990  
 The degree of waste waters decontamination from mercury varied between 25.8 and 99.68%. The level of mercury in purified waste water was between 0.1 and 5.88 mg/dm<sup>3</sup>

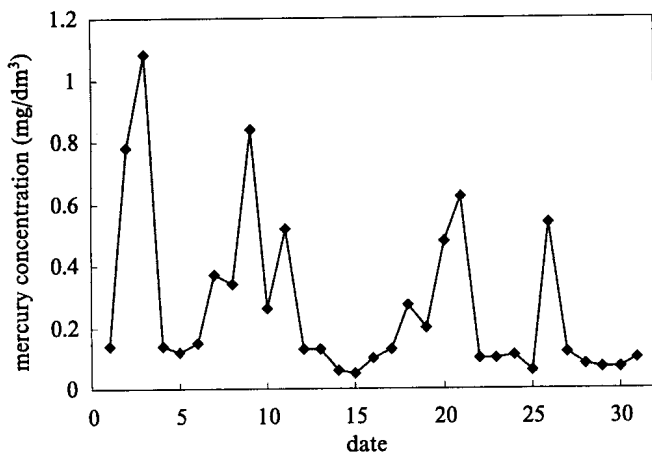


**Table 2.** Results of study of the purification treatment efficiency and control of mercury levels in watercourse for June of 1990

Date	At the facilitie's entry		At the facilitie's exit		Purification effectivity % E	At the entry to the watercourse	
	water	mass	water	mass		water	mass
	volume, Q (m <sup>3</sup> /day)	Hg (kg/day)	volume, Q (kg/day)	Hg (kg/day)		volume, Q (m <sup>3</sup> /day)	Hg (kg/day)
1						2670	1.682
2	120	3.83	120	0.08	97.91122715	2600	0.078
3						2560	0.307
4						2470	2.47
5						2460	3.075
6						2490	1.345
7						2500	3.8
8						2560	0.563
9						2520	0.151
10						2720	0.082
11						2560	0.768
12	60	1.14	60	0.06	94.73684211	2660	1.702
13	60	0.37	60	0.03	91.89189189	2740	1.754
14	130	1.71	130	0.057	96.66666667	2770	3.656
15	130	1.25	130	0.067	94.64	2770	0.194
16	120	0.68	120	0.113	83.38235294	2780	0.89
17	50	0.82	50	0.037	95.48780488	2650	0.265
18	60	0.19	60	0.141	25.78947368	2700	1.134
19	130	0.84	130	0.031	96.30952381	2810	1.236
20	60	0.1	60	0.006	94	2820	1.918
21	60	0.53	60	0.009	98.30188679	2760	3.312
22	120	1.86	120	0.032	98.27956989	2860	0.343
23	140	0.32	140	0.04	87.5	2640	1.003
24	60	1.89	60	0.006	99.68253968	2570	1.799
25	70	4.8	70	0.063	98.6875	2590	3.419
26						2440	0.293
27						2500	0.15
28						2440	0.098
29						2480	14.592
30						2440	7.027
Total						78530	59.11

**Table 3.** Results of study of the purification treatment efficiency and control of mercury levels in watercourse for January of 1991

Date	At the facilitie's entry		At the facilitie's exit		Purification effectivity % <i>E</i>	At the entry to the watercourse	
	water	mass	water	mass		water	mass
	volume, <i>Q</i> (m <sup>3</sup> /day)	Hg (kg/day)	volume, <i>Q</i> (kg/day)	Hg (kg/day)		volume, <i>Q</i> (m <sup>3</sup> /day)	Hg (kg/day)
1	60	0.64	60	0.105	83.59375	2610	0.365
2	60	1.07	60	0.048	95.51401869	2670	2.083
3	60	0.86	60	0.009	98.95348837	2590	2.797
4	60	1.48	60	0.138	90.67567568	2610	0.365
5						2610	0.313
6	70	1.38	70	0.054	96.08695652	2650	0.398
7	60	2.58	60	0.033	98.72093023	2610	0.966
8	70	4.17	70	0.007	99.83213429	2660	0.904
9	60	2.67	60	0.141	94.71910112	2630	2.209
10	60	3.28	60	0.035	98.93292683	2670	0.694
11	60	2.37	60	0.043	98.18565401	2590	1.347
12						2580	0.335
13	60	1.83	60	0.091	95.0273224	2610	2.949
14	60	1.47	60	0.088	94.01360544	2580	0.16
15	60	0.98	60	0.057	94.18367347	2700	0.14
16	60	0.31	60	0.01	96.77419355	2640	0.264
17						2520	0.328
18	60	0.63	60	0.028	95.55555556	2590	0.699
19	60	0.82	60	0.086	89.51219512	2550	0.51
20	50	0.22	50	0.042	80.90909091	2580	1.238
21						2730	1.693
22						2650	0.265
23	60	1.4	60	0.042	97	2760	0.275
24	60	1.77	60	0.019	98.92655367	2730	0.3
25	60	2.01	60	0.04	98.00995025	2550	0.153
26	60	1.65	60	0.035	97.87878788	2700	1.458
27						2670	0.32
28						2530	0.202
29	60	1.57	60	0.319	79.68152866	2520	0.176
30						2640	0.185
31						2620	0.262
Total	1330	35.15	1330	1.47	95.81792319	81340	24.356



**Fig. 9.** Mercury concentrations in waste waters at the watercourse entry in January of 1991. The degree of waste waters decontamination from mercury varied between 83.6 and 99.8%. The level of mercury in purified waste water was between 0.1 and 2.11 mg/dm<sup>3</sup>

## CONCLUSIONS

From the results presented above some concluding remarks may be drawn:

- Method of flameless AAS can be reliably used for determination of mercury in chlorine-alkali electrolysis waste waters.
- Concentrations of Hg(II) in water entering a watercourse show a good treatment of waste waters, even though these concentrations were increased.
- Taking into account the fact that mercury takes part in a series of complex reactions which can even lead in its accumulation in certain location, it is necessary to carry out an additional research of river sediment and its basin in order to give valid evaluation of the degree of pollution.
- Even though the details are shown for 1990 and 1991, they can also be compared with average values for the efficiency of waste water purification in 1996 and 1997. The data comparison is given in Table 4.

**Table 4.** Trend in the efficiency of waste water purification from 1990-1997

Year	Average efficiency of purification plants (%)
1990	35-98.9
1990	26-99.7
1991	84-99.8
1996	80-98
1997	78-99.1
1998	82-98.9

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