

On the Choice of Working Conditions for the Determination of Trace Elements in the Composition of Sediments of Waste Waters of City Purification Plants

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Abstract

Various conditions of extraction of chemical elements (Cd, Zn, Cu, Cr, Mn, Pb, Ni, As, Hg) standardized in the composition of sediments of waste waters of urban purification works for their subsequent assay by the method of atomic absorption recommended for production control and estimation of sediments hazard class have been studied. It is demonstrated that the maximal extraction of Cd, Zn, Cu, Cr, Mn, Pb and Ni is achieved when using a mixture of nitric acid and hydrogen peroxide for heating. A special preparation of samples is recommended for extraction of Hg and As. Taking into account the results obtained with the help of the method proposed, the hazard class of real waste water sediments of urban purification works of Kazan and Naberezhnye Chelny has been calculated, and the possibility of their use as fertilizer has been estimated.

INTRODUCTION

The development of industry and public utilities increases water consumption and, as a consequence, the formation of wastes in the form of sewage. Their purification at urban purification works entails an increase in the amount of waste water sediments (WWS) which have a multicomponent composition that is continuously changing due to the activity of microorganisms [1]. The bulk of the sediments is represented by natural compounds, however, their composition includes also substances having toxic properties. Heavy metals (HM) which WWS content varies within a wide range, mg/kg: Zn 150–8000, Cu 150–4000, Pb 52–600, Cd 3–165, Cr 225–4200, Ni 3–1400 belong here [1]. Besides, the sewage water sediments often contain toxic organic compounds, such as benz(a)pyrene, N-nitrosodiethyl- and N-nitrosodimethyl amine, pesticides (aldrin, dieldrin, chlordan, lindan, DDT + DDD), polychlorinated

biphenyls, aromatic compounds of phenol series *etc.* [1–4]. All this makes the solution of the WWS utilization problem very difficult. The ecologically most acceptable way of using WWS as fertilizers contributes to return of chemical elements to the natural circulation, however, its implementation is determined by the content of toxic elements which can considerably exceed the permissible standards safe for the soil – plant system [5]. Other methods of WWS utilization are burning, burying *etc.* The choice of optimal WWS utilization method must be preceded by a thorough analysis of chemical composition on which the estimation of its hazard class has to be based [6–9].

The most important tasks associated with the solution of this problem include, as it was noted earlier [1], development of standardized techniques of assay of chemical composition taking into account the matrix of the samples to be controlled for a reliable estimation of quality of the formed sediments, and the de-

gree of their influence on contiguous media. Usually, in estimation of pH, humidity, organic carbon content and other agronomic WWS indices, GOSTs recommended for analysis of fertilizers [9–12] are used. For assay of toxic elements in WWS, methods destined for analysis of soils and vegetable products with variants of preliminary extraction of the elements to be assayed are used [13]. So, the preliminary chemical degradation of the sample is made with solution of nitric acid (1 or 5 M), concentrated sulphuric and hydrofluoric acids, aqua regia, nitric and chloric acids. Often, oxidation is accompanied by boiling, autoclave treatment, incineration in muffle furnace or decomposition in a microwave furnace. The metal content after the treatment is estimated by means of atomic absorption or atomic emission [14–31].

The goal of the present study was the choice of optimal working conditions for assay of elements in WWS formed at purification works of large cities using atomic absorption spectroscopy (AAS) recommended for industrial control, and estimation of hazard of sewage waters of Kazan' and Naberezhnye Chelny (Republic of Tatarstan).

EXPERIMENTAL

Waste water sediments from purification plants of two large cities – Kazan' and Naberezhnye Chelny – were used as investigation objects. In the two cases, both fresh sediments and WWS stored on silt maps were studied; the sediments from silt maps of Kazan had been stored for 20 years, those from maps of Naberezhnye Chelny had been stored for 5 years.

Samples of sewage water sediments distributed on silt maps were taken according to the "envelope" method (four point samples at the corners and one at the center of a square with sides of 25 m), and when this was not possible, samples were taken from the perimeter of the map every 10 m. The samples were taken from the surface (0–20 cm) or layer-by-layer at the depths of 30–60, 60–90, 90–120 and 120–150 cm, the mass of the sample at each point being 0.1–0.3 kg [3]. In cases of high moisture of the sewage water sediment, sampling was made with the help of samplers.

A pooled sample of WWS with a mass of not less than 1 kg was prepared according to the principle of weighted average or geometric mean, depending on the sample humidity. A pooled sample of solid and paste-like sediments with a moisture of 30 to 70 % is formed by mixing equal mass fractions of the substance according to the weighted average principle. A pooled sample of semiliquid and dough-like sediments with a high moisture (>70 %) is prepared according to the average proportionality principle from sediments of equal volume. A WWS sample was dried to air-dry condition, crushed and sifted through a sieve with $d = 1$ mm.

For extraction of HM, the sediments were treated as follows:

- 1) with 1 M HNO_3 solution according to [13];
- 2) with 5 M HNO_3 solution according to [14];
- 3) with a mixture of HNO_3 and HClO_4 (70 : 30) with heating [18];
- 4) successively with HNO_3 (1 : 1) and 30 % H_2O_2 with heating for 10 min [13];
- 5) with concentrated HNO_3 and 30 % H_2O_2 with heating during 4 h with subsequent autoclave (microwave) degradation [28–30];
- 6) with aqua regia (mixture of HNO_3 and HCl (1 : 3) with heating [21];
- 7) mineralization of products of biological origin, according to All-Union State Standard [27];
- 8) dry incineration of samples at $T = 400$ – 450 °C in a muffle oven with subsequent dissolution in a mixture of HF , HClO_4 and HCl [21];
- 9) dry incineration of samples at $T = 400$ – 450 °C in a muffle oven with subsequent dissolution in HNO_3 [16].

Assay of elements in solutions was performed on atomic absorption spectrometers C-600 and AAS-3. The chance component of the measurement error was estimated according to All-Union State Standard [32]. Nine replications of the procedure were made. Comparison of measurement results was made by the Student test [33].

RESULTS AND DISCUSSION

At the first stage, WWS samples were preliminarily characterized with respect to the pH

TABLE 1
Agrochemical indices of waste water sediments

Index	Recently precipitated sediments		Sediments from silt maps	
	Kazan'	Naberezhnye Chelny	Kazan'	Naberezhnye Chelny
pH (salt)	6.9	7.0	7.5	7.1
Moisture, %	88	79	70	72
C _{org} , %	60	61	25	51
P _{tot} , %	3.0	2.5	2.8	2.0
N _{tot} , %	1.2	1.0	1.0	0.8
K _{tot} , %	0.30	0.46	0.38	0.44

value of the salt extract, its moisture and organic substance content. As one can see from the results presented in Table 1, the largest variation was observed in the organic carbon content (25 to 61 %); that of nitrogen, phosphorus and potassium varied only slightly. The sediments had a neutral reaction (pH 6.9–7.1) and a high moisture (70 to 88 %).

On the whole, the values of parameters characterizing the agrochemical properties of sediments were traditional of sewage water sediments of large industrial cities [1–4]. A comparison of the results obtained demonstrates that recently precipitated sediments contain more organic substance as estimated by the organic carbon (C_{org}) than WWS stored on silt maps do. This is accounted for by the fact that in the process of storage of sediments on silt maps decomposition of organic substance takes place, which is the most pronounced in the case of sediments in Kazan'.

The toxic element content of WWS is presented in Tables 2–6.

As witnessed by the data of Table 2, by the methods 8 and 9 a smaller amount of Cd is extracted from recent sediments of Kazan' (Kaz_{rec}) (16.0 and 16.5 mg/kg, respectively) than by the methods 1–7 (19.5 to 21.0 mg/kg). Therein a significant difference ($P < 0.05$) in the content of Cd extracted by the methods 8, 9 and 1–7 was found. A similar pattern in WWS analysis was found when analyzing the WWS from silt maps of purification plants of Kazan' (Kaz_{map}) and Naberezhnye Chelny (NC_{map}) (see Tables 3 and 5), the data obtained being not significantly different. Cadmium content of recently precipitated sediments from Naberezhnye Chelny (NCh_{rec}) (see Table 4) extracted by

the methods 8 and 9 differs significantly from that extracted by methods 5 and 7. When other extraction techniques were used, no significant differences were found. As one can see from the results obtained, all the methods except for 8 and 9 make it possible to extract equal amounts of cadmium. The poorer efficiency of methods 8 and 9 seems to be accounted for by the partial loss of cadmium at temperatures higher than 400 °C due to volatility of some of its compounds, which is in accordance with literature data [26].

The highest zinc content of Kaz_{rec} (see Table 2) was found when using extraction methods 2–7. No significant differences in the content of zinc extracted by these methods were found. A smaller amount of Zn was obtained when using methods 1, 8 and 9, there being no significant differences between the results obtained by techniques 2, 8 and 9. Zinc can be extracted rather efficiently by various methods, the most so by methods 5 and 7. The methods which use permits extracting a significantly smaller amount of zinc include method 1 (for all sediments), 8 and 9 (NCh_{rec}, NCh_{map}, Kaz_{map}).

The maximal amount of lead can be extracted from Kaz_{rec} using methods 3 and 5, from Kaz_{map} using method 5, in analysis of NCh_{rec} for lead the maximal result is given by methods 2–7, in that of NCh_{map} by 3–7 (see Tables 2–5). A significantly smaller amount of lead has been found with preliminary treatment of all samples by methods 8 and 9, like in assay of Cd. Noteworthy is the fact that in the case of Kaz_{rec}, NCh_{rec} and NCh_{map} sediments, the lead was extracted equally intensely by several methods, whereas from Kaz_{map} sample only by method 5. The latter may caused

TABLE 2

Metal content of recently precipitated WWS of Kazan', mg/kg, and the chance component of measurement error (in brackets)

Method of extraction*	Cd	Zn	Cu	Cr	Mn	Pb	Ni	K
1	19.5(2.3) a**	1470(194) a	192(25) a	1180(112) a	360(32) a	79(9) a	1000(90) a	
2	20.0(2.6) a	2000(280) bc	235(28) b	1270(177) ab	400(40) a	87(10) ab	1060(90) a	
3	20.0(2.0) a	2257(299) b	350(38) c	1390(208) bd	594(45) b	92(9) bc	1280(90) b	
4	20.0(2.1) a	2300(345) b	290(30) bd	1380(200) bd	520(59) b	91(8) abc	1200(117) ab	
5	20.0(2.0) a	2350(282) b	370(34) bd	1390(204) ab	600(50) b	98(9) cb	1320(140) bc	28.65163
6	21.0(2.2) a	1890(195) bc	290(35) d	1250(160) ab	560(45) b	85(7) ab	1040(83) a	
7	20.0(2.1) a	2300(269) b	350(42) c	1300(182) ab	580(60) b	80(8) ab	1260(113) bc	
8	16.0(1.8) b	1780(214) c	360(27) cd	1390(180) b	605(50) c	70(7) a	1300(116) c	
9	16.5(2.0) b	1800(216) c	360(30) c	1400(168) b	610(55) c	75(7) a	1310(117) c	
<i>Standard</i>								
<i>content</i> [5]	30	4000	1500	1200	2000	1000	400	

*See in the text.

**Results with the same letters between average measures have no significant differences according to Student test.

TABLE 3

Metal content of WWS from silt maps of purification works of Kazan', mg/kg, and the chance component of measurement error (in brackets)

Method of extraction	Cd	Zn	Cu	Cr	Mn	Pb	Ni	K
1	15.9(1.8) a	1312(157) a	634(82) a	1200(150) a	300(27) a	91(9) a	912(91) a	
2	17.0(2.0) a	1420(156) ab	705(78) a	1700(183) b	304(28) a	106(9) b	1086(98) ab	
3	17.2(2.4) a	1650(214) bc	840(84) b	1800(260) b	397(35) bc	129(10) c	1200(108) bc	
4	17.1(2.4) a	1600(188) bc	700(70) ac	1800(240) b	300(31) bc	116(10) bc	1112(95) c	
5	17.0(2.4) a	1670(184) c	850(102) b	1850(252) b	400(32) bc	130(10) c	1310(108) c	39.95335
6	17.0(2.6) a	1620(175) dc	800(80) bc	1810(262) b	350(32) b	115(11) bc	1100(106) b	
7	17.5(3.2) a	1680(202) c	820(74) b	1800(224) b	400(36) bc	125(12) bc	1200(94) b	
8	14.0(1.4) b	1300(158) a	810(70) b	1800(224) b	410(37) bc	80(7) a	1300(100) c	
9	13.8(1.6) b	1420(219) ab	820(82) b	1830(230) b	420(34) c	80(8) a	1320(122) c	
<i>Standard</i>								
<i>content</i> [5]	30	4000	1500	1200	2000	1000	400	

Notes the same as in Table 2.

TABLE 4

Metal content of recent sediments of WWS from Naberezhnye Chelny, mg/kg, and the chance component of measurement error (in brackets)

Method of extraction	Cd	Zn	Cu	Cr	Mn	Pb	Ni	K
1	3.08(0.38) ab	1337(101) a	71(7) a	164(20) a	200(18) a	30(3) a	98(11) a	
2	3.08(0.38) ab	1430(143) ab	102(9) b	185(24) ab	222(20) a	41(3) b	100(9) a	
3	3.30(0.41) ab	1530(200) ab	116(10) c	210(25) ab	257(26) bc	45(4) b	124(11) b	
4	3.30(0.41) ab	1587(235) ab	112(13) c	200(30) ab	240(21) bc	41(4) b	130(13) b	
5	3.4(0.54) a	1580(200) b	120(11) c	240(36) b	260(26) bc	46(4) b	138(12) b	9.206843
6	3.4(0.54) a	1360(160) ab	112(10) c	200(31) ab	223(22) ab	40(3) b	132(14) b	
7	3.0(0.50) ab	1500(200) ab	120(12) c	225(33) b	250(23) bc	44(4) b	136(14) b	
8	2.6(0.39) b	1300(155) a	122(12) c	220(26) b	270(27) cb	32(3) a	132(12) b	
9	2.6(0.40) b	1300(172) a	125(13) c	220(26) b	260(23) cb	29(3) a	138(12) b	
<i>Standard</i>								
<i>content</i> [5]	30	4000	1500	1200	2000	1000	400	

Notes the same as in Table 2.

TABLE 5

Metal content of WWS from the silt maps of purification works of Naberezhnye Chelny, mg/kg, and the chance component of measurement error (in brackets)

Method of extraction	Cd	Zn	Cu	Cr	Mn	Pb	Ni	K
1	5.0(0.6) a	1910(229) a	64(8) a	62(10) a	234(20) a	74(7) a	100(10) a	
2	5.4(0.6) a	2200(286) ac	82(9) b	98(12) b	376(33) b	90(8) b	109(10) ac	
3	5.6(0.7) a	2870(316) b	180(18) c	100(15) b	565(44) c	110(9) b	145(13) b	
4	5.6(0.7) a	2900(319) b	100(14) d	100(14) b	500(50) c	100(10) b	120(11) c	
5	5.6(0.8) a	2900(319) b	180(16) c	102(16) b	580(55) cd	112(9) bc	150(15) b	13.62221
6	5.4(0.6) a	2900(348) b	170(15) c	100(11) b	560(50) c	111(10) b	115(12) ac	
7	5.6(0.9) a	2600(310) bc	168(20) c	90(9) b	560(50) c	114(10) b	140(12) b	
8	4.0(0.4) b	1800(234) a	170(14) c	95(9) b	660(66) d	75(8) a	142(13) b	
9	4.0(0.5) b	1800(216) a	172(15) c	100(11) b	665(66) d	72(7) a	140(13) b	
<i>Standard</i>								
<i>content</i> [5]	30	4000	1500	1200	2000	1000	400	

Notes the same as in Table 2.

TABLE 6
Mercury and arsenic content of WWS samples, mg/kg

Waste water sediment	As	Hg
Recent		
Kazan'	<1	0.06 ± 0.01
Naberezhnye Chelny	<1	0.08 ± 0.02
Silt maps		
Kazan'	<1	0.41 ± 0.08
Naberezhnye Chelny	<1	0.45 ± 0.09
Standard		
content [5]	20	15

by a longer storage of the sediment of Kaz_{map} and by a stronger binding of metals with the sediment matrix in the process of transformation with participation of microorganisms.

The lowest copper content was found in samples with the use of only method 1. From samples of Kaz_{rec} and Kaz_{map} copper was maximally extracted by methods 3, 5, 8, 9, and for those of NCh_{rec} and NCh_{map} these methods were joined by 6 and 7, which, probably like in the case of lead, was due to the time of storage of the sediment on silt maps.

The data presented in tables 2–5 demonstrate that the chromium content as estimated by methods 2–9 varies depending on the method and on the sediment sample; however, these differences are mostly non-significant. A significantly lower chromium content in WWS was found only when method 1 was used.

Methods 1 and 2 turned out to be poorly efficient in manganese extraction from all the samples, and method 9 was the most efficient. For sediments of NCh_{rec}, NCh_{map} and Kaz_{rec}, methods 5 and 8 may be added.

Analogous patterns have been noted also when extracting nickel: methods 1 and 2 were the least efficient, and methods 5, 7–9 the most efficient. In the cases of NCh_{rec} and NCh_{map} sediments, methods 3 and 4 may also be used. Nickel forms highly stable complexes with oxygen-, nitrogen- and sulphur-containing ligands [21], and therefore for its extraction from an organomineral WWS matrix stronger oxidants (hydrogen peroxide, perchloric acid) and a long-term (for 3 h) heating are necessary. Method of dry incineration of WWS is also acceptable.

In this way, analysis of the content of elements extracted by various methods shows that, firstly, the range of efficient methods of extraction of elements from freshly precipitated sediments is wider than the techniques acceptable for stored sediments; secondly, the optimal method permitting an efficient extraction of all elements is method 5. It is just this method that may be recommended for carrying out mass analyses in the process of control of SWS samples.

In quantitative estimation of such elements as arsenic and mercury, which are also standardized in the WWS composition (As – 20 mg/kg, Hg – 15 mg/kg [5]), a special preparation of samples is necessary which differs from that described above for HM. The use of hydrochloric acid for extraction of arsenic and mercury from WWS samples gives considerably decreased results due to the formation of volatile chlorides of As (III) and Hg (II) [34]. Mercury can be extracted especially completely with a mixture of nitrous and sulphuric acids during heating to 60–70 °C. For a complete degradation of organic substance in an WWS sample one has to use a solution of potassium permanganate and potassium persulphate. At higher temperatures, the oxidation reaction goes very intensely, and the loss of mercury occurs due to the volatility of its compounds [34]. The best results have been obtained by means of atomic absorption with the help of additions.

We have estimated the possibility of using the samples studied as a fertilizer in agriculture. When comparing the data obtained by method 5 with those presented in Sanitary Rules and Standards [5], it was found that the use of WWS from Kazan' as a non-traditional fertilizer was limited by the presence of excess of chromium (1400 and 1800 mg/kg) and nickel (1300 and 1200 mg/kg). The content of standardized toxic elements in WWS from Naberezhnye Chelny does not exceed the limit values established in the Sanitary Rules and Standards [5]; therefore, these sediments are not dangerous and may be used as fertilizers in agriculture.

Waste water sediments represent a peculiar kind of production and consumption wastes, and therefore their storage and disposal are

determined according to their hazard class. As a result of calculations, it has been established that the hazard index of samples of Kaz_{rec} , Kaz_{map} , NCh_{rec} and NCh_{map} have the following values: 35.05, 39.95, 9.21 and 13.62, respectively. Hence, the sediments of Kaz_{rec} , Kaz_{map} and NCh_{map} may be considered as belonging to class 4 (slightly hazardous), whereas the sediment of NCh_{rec} as belonging to class 5 (practically non-hazardous). The belonging of sediments to hazard class has been confirmed, as it is required, by independent results of biological testing of samples on crustaceans *Daphnia magna* and protozoa *Paramecium caudatum* [2] (the data are not presented here).

CONCLUSIONS

Various conditions of extracting Cd, Zn, Cu, Cr, Mn, Pb, Ni, As and Hg from waste water sediments from city purification plants for subsequent estimation of their content by means of atomic absorption for the purpose of mass production control and determination of their hazard class have been studied. Maximal extraction of Cd, Zn, Cu, Cr, Mn, Pb and Ni was achieved with the use of a mixture of nitric acid and hydrogen peroxide with heating. For extraction of Hg and As, a mixture of nitrous and sulphuric acids with heating is recommended, and the best results were obtained with the help of atomic absorption technique using additions. The level of toxic element content of real waste water sediments formed at purification plants of Kazan and Naberezhnye Chelny has been estimated, their hazard class has been determined, and the possibility of their use as fertilizers has been studied.

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