DETERMINATION OF Hg(II) IN DRINKING WATER BY ATOMIC ABSORPTION SPECTROMETRY — COLD VAPOUR METHOD AFTER CONCENTRATION BY COLUMN EXTRACTION CHROMATOGRAPHY

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The method describes concentration of mercury in samples of drinking water from water mains with Hg concentration above $1{\cdot}0 \,.\, 10^{-7}\,\mathrm{g\,l^{-1}}$ ($5{\cdot}0 \,.\, 10^{-10}\,\mathrm{mol\,l^{-1}}$) by means of extraction chromatography on a column packed with a carrier Synachrom E-5 wetted with saturated solution of bis(diethyldithiocarbamate)copper(II) complex in 1 : 1 mixture 1,2-dichlorobenzene + + cyclohexane. After elution with $3{\cdot}0\,\mathrm{mol\,l^{-1}}$ HCl the mercury concentration in the eluate is determined by atomic absorption spectrometry — cold vapour method. Average yield of the mercury separation from the model solutions was 95·8%.

Mercury, lead, and cadmium form a triad of the most toxic elements whose content in drinking water and water-works supplies is followed[1]. The method prescribed by standards[2] — AAS — cold vapour method — can determine directly the concentrations above $5{\cdot}0 \,.\, 10^{-7}\,\mathrm{g\,l^{-1}}$, *i.e.* $2{\cdot}5 \,.\, 10^{-9}\,\mathrm{mol\,l^{-1}}$ (ref.[3]). The maximum admitted mercury content in water-works supplies is $5{\cdot}0 \,.\, 10^{-10}\,\mathrm{mol\,l^{-1}}$ (ref.[4]), so analytical control of water-works supplies necessitates an at least five-fold concentrating of the samples.

So far the following concentration procedures of the metals (with subsequent determination by AAS) have been recommended: extraction of the dithiocarbamate complexes with organic oxygen-containing solvents (*e.g.* methyl-isobutyl ketone)[5-9] with subsequent direct determination of the metal in the organic phase; extraction of the dithiocarbamate complexes with oxygen-containing or chlorinated organic solvents (*e.g.* MIBK, $CHCl_3$, CCl_4) and subsequent reextraction of the metal with nitric acid and analysis of the acidic extract (water phase)[10-14]. Lo and coworkers[15] use for the reextraction an exchange reaction of Hg(II) in HNO_3 with the dithiocarbamate complexes of the metals; reduction of Hg(II) with $SnCl_2$ and transfer of mercury by inert gas to a receiver containing a solution of $KMnO_4$ and H_2SO_4 (ref.[16-18]); trapping of Hg vapours by gold or silver on suitable carriers (the so called amalgamators)[19-24]; trapping of Hg vapours on MnO_2 (ref.[25,26]); extraction chromatography (RPPC (ref.[27-30])).

Earlier communications[31-34] used the labelled metal compounds (^{203}Hg, ^{60}Co, ^{65}Zn, ^{125}Sb, ^{110m}Ag, ^{55}Fe, ^{207}Bi, and ^{75}Se) and the methods of scintillation and Ge (Li) semiconductor gamma-spectrometry to studies of various carriers, their grain size, elution reagents, effects of flow rate of liquids through the column during sorption and elution, effect of pH of the solutions and that of the presence of other metals in the sample on the separation of Hg(II) by means of RPPC. These studies used various organic solvents or mixtures for preparation of the stationary phase, tried to find the optimum dimensions of the columns, and investigated their service life during repeated separation cycles.

The aim of the present work was to find a suitable separation procedure enabling separation and concentration of Hg(II) from samples of drinking water from water-works supplies containing more than $5{\cdot}0 \,.\, 10^{-10}$ mol l^{-1} and subsequent determination of Hg(II) by AAS – cold vapour method.

EXPERIMENTAL

Reagents and Apparatus

The reagent — bis(diethyldithiocarbamate)copper(II) complex ($Cu(dedtc)_2$) — was prepared according to Vašák & Šedivec[35], m.p. 194·5°C, ε_{max} (434 nm) = 12 680 l mol^{-1} cm^{-1}. The standard solution of $1{\cdot}0 \,.\, 10^{-2}$ mol l^{-1} $Hg(NO_3)_2$ was prepared from solid HgO and standardized by titration on NaCl. Carrier of the stationary phase — Synachrom E-5 (Research Institute of Synthetic Resins and Lacquers, Pardubice) $d_p = 0{\cdot}125-0{\cdot}160$ mm. All the chemicals used were of *p.a.* purity grade (Lachema Brno, ČSSR and Laborchemie Apolda, DDR). The extraction chromatography unit was constructed by us. We also used a peristaltic pump type 315 (Zalimp, Poland) and an atomic absorption spectrometer Perkin-Elmer Model 603 (Bodenseewerk, BRD) with accessory equipment MHS-1.

Preparation and Packing of the Columns

Glass columns 200 × 8 mm with sintered glass S-1 were degreased in chromosulphuric acid, dried, and immersed in 3% (v/v) solution of methylsilicone oil in xylene for 24 h, and finally heated at 300°C in an electric oven for 10 h.

The carrier of stationary phase was shaken with saturated solution of $Cu(dedtc)_2$ in a 1 : 1 mixture of 1,2-dichlorobenzene + cyclohexane (15 ml of the solution per 1 g of the carrier) for 2 h, where after the mixture was left to stand in the dark for 6 days. The columns were packed with the impregnated carrier with simultaneous evacuation (oil pump). The packed columns were wrapped in aluminium foil to prevent undesirable effects of light. Before use the columns were washed with 250 ml distilled water and submitted to three separation cycles to verify their function.

Procedures

The sorption of Hg(II) from 1 l sample was carried out on the column with the flow rate $F_m = 12$ ml min^{-1}. The elution was completed with 50 ml HCl ($c_{HCl} = 3{\cdot}0$ mol l^{-1}; $F_m = 1{\cdot}5$ ml . min^{-1}). The eluate was collected in 100 ml calibrated flask, stabilized with 1·0 ml conc. HNO_3 and 0·2 ml 5% $K_2Cr_2O_7$[2], and the volume was adjusted by addition of distilled water. After the elution was finished, the column was washed with 50 ml distilled water and so prepared for a subsequent separation cycle.

For determination of Hg content 25 ml of the eluate was treated with 1·0 ml conc. H_2SO_4 and 0·5 ml conc. HNO_3. The determination was carried out by the AAS — cold vapour method using $SnCl_2$ as the reducing agent at the wavelength 253·7 nm.

The Blank Test and Limitations of the Method

For the blank test we used 25 ml distilled water with addition of 1·0 ml conc. H_2SO_4, and 0·5 ml conc. HNO_3, the procedure being the same as above. Ten experiments were used for calculation of the mean value of the blank test $\bar{x}_0 = 6{\cdot}77$ ng Hg ($s = 1{\cdot}27$ ng Hg). From these values we calculated the detection limit x from the relation

$$x = \bar{x}_0 + \omega s \qquad (1)$$

for $\omega = 3$ and the volume 25 ml, hence the detection limit for the whole sample volume (1 000 ml) is $x = 423{\cdot}2$ ng Hg.

The Hg content in the elution reagent used ($c_{HCl} = 3$ mol l^{-1}) was determined by the AAS – cold vapour methods. The mean value calculated from 15 experiments was 1·38 ± 0·03 µg Hg per 1 l HCl ($\alpha = 0{\cdot}05$). This value was subtracted from the individual results.

RESULTS

To verify the recovery of the procedure we prepared artificial samples from distilled water by addition of Hg(II) to overall concentrations of 1 000, 500, and 100 ng l^{-1}. The mercury contained in these samples was separated on the column and determined, the results are summarized in Table I.

The method was also applied to 5 samples of drinking water from water mains of the town Pardubice. The Hg(II) separation was carried out simultaneously using 5 parallel columns. The results are given in Table II.

DISCUSSION

The detection limit of Hg(II) by AAS – cold vapour method was determined[36] as a sum of the mean value of blank test ($\bar{x}_0$) and triple value of assessed standard

TABLE I

Determination of Hg(II) in model samples by AAS after separation on a column

Given Hg		n^a	Found	s^b	$L_{1/2}^c$	Δ^d	$t_{calc.}$	$t_{crit.}$	S_r^e	L_r^f
ng l^{-1}	mol l^{-1}		ng l^{-1}	ng l^{-1}		%	($\alpha = 0{\cdot}05$)		%	%
1 000·0	$5{\cdot}0 \,.\, 10^{-9}$	25	947·9	74·0	±30·5	−5·2	1·708	2·060	7·8	6·4
500·0	$2{\cdot}5 \,.\, 10^{-9}$	50	476·4	43·4	±12·3	−4·7	1·919	2·008	9·1	5·2
100·0	$5{\cdot}0 \,.\, 10^{-10}$	30	95·8	10·8	± 4·0	−4·2	1·050	2·042	11·3	8·3

[a] Number of the determinations; [b] estimate of standard deviation; [c] the confidence interval for $\alpha = 0{\cdot}05$; [d] the relative error of the determination; [e] relative standard deviation; [f] the relative error of the confidence interval.

deviation (s). This way of evaluation of the detection limit disagrees with the suggestion of the ACS commission[37] which recommends that the signal of the determined substance be taken as a detection region within the interval of the values 3 – 10 s, and only the signal larger than 10 s can be considered as the region of determinability.

In accordance with the two communications[36,37] and on the basis of our own experiments it can be stated that the AAS – cold vapour method enables direct determination of Hg(II) in drinking water, *i.e.* at the concentrations of about 1 μg per 1 l of the sample[1], but it does not enable direct determination of Hg(II) in water-works supplies, *i.e.* at the concentrations about 100 ng Hg per 1 l of the sample[4], because the aliquot sample volume 25 ml necessary for one analysis only contains about 2·5 ng Hg which is below the detection limit. Therefrom it follows inevitably that analytical control of water-works supplies will require an at least five-fold concentrating of the sample.

This requirement initiated studies of column separations of Hg(II) which are dealt with in several previous communications[31–34]. Results of these studies were summarized to develop a method of Hg(II) separation by extraction column chromatography with simultaneous concentration of the analyte.

Correctness of the results of determination of Hg(II) by AAS in the model samples after separation in a column with simultaneous concentration of Hg was evaluated by the Student test[36]. In all the cases it was found that $t_{\mathrm{calc}} < t_{\mathrm{critical}}$, hence the dif-

TABLE II

Determination of Hg(II) in drinking water by AAS after separation on a column

Found Hg $\mathrm{ng\,l^{-1}}$	n[a]	s $\mathrm{ng\,l^{-1}}$	$L_{1/2}$ $\mathrm{ng\,l^{-2}}$
60·6[b]	5	7·0	8·7
44·6[b]	5	10·0	12·5
46·0[b]	5	5·4	6·7
37·6[b]	5	0·9	11·0
23·1[b]	5	10·0	12·4
51·8[c]	5	3·5	4·4
29·7[c]	5	5·2	6·4
15·6[c]	5	3·3	4·1
9·5[c]	5	3·3	4·1
13·2[c]	5	2·7	3·3

[a] For the symbols see Table I. [b] Distilled water. [c] Drinking water; all the values are lower than the maximum content allowed by[4].

ference $|\bar{x} - \xi|$ (where ξ means the real value) is statistically insignificant and can be only explained by random errors of the analysis.

Accuracy of the results of Hg(II) determination by AAS in the model samples after column separation with simultaneous concentration of Hg was evaluated by means of relative standard deviation (which exceeded the 10% value for the lowest given Hg amount (100 ng l^{-1}) only) and relative width of the confidence interval (which did not exceed the value of 10% for all three given Hg amounts in the model samples).

Identity of results of the separations carried out simultaneously on five various columns, *i.e.* statistical significance of difference of two average values, was tested by the Student test of coincidence of two mean values[36]. No statistically significant difference has been found between the separations of model samples carried out on five parallel columns.

The results of Hg(II) determinations in the model samples showed unambiguously that the developed procedure of Hg separation on a column with simultaneous Hg concentration and subsequent determination of Hg by the AAS – cold vapour method enables reliable analytical control of Hg content in drinking water from water-works supplies.

As compared with the other separation procedures given in the Introduction, our method enables to carry out parallel separations from several samples (up to 15 samples at the same time, if the Zalimp 315 peristaltic pump is used), the whole Hg separation from a 1 l sample lasting less than 150 min.

With respect to the fact that the AAS – cold vapour method attains the lowest detection limit of Hg in liquid samples (as compared with other analytical methods), it was impossible to check quality of the separation process in the column by another analytical method.

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