Activation Analysis of Mercury in Urine Samples of Electrolysis Cell Workers

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The activation method of determination of trace amounts of Hg in human urine has been studied by introducing a simple amalgam deposition method. Human urine samples were obtained from the alkali chloride electrolysis plant equipped with Hg cells. The capacity of Cu powder for Hg quantity, the pH conditions, and the shaking time were described. The results showed that the Hg contents in workers' urine samples varied from 33 ppb to 600 ppb depending on working conditions.

1. Introduction

The manufacture of soda ash, caustic soda and chlorine by amalgam mercury cells of electrolytic production method is one of the most important heavy chemical industries.

Mercury is a volatile and poisonous element. The determination of mercury in urine of workers is of great importance in the evaluation of health hazards. Chen, et al.¹⁾ found that Hg content in worker's hair varied from 20 to 300 ppm. The determination of mercury in various matrices can be performed with different analytical methods.^{2)~5)} Recently a review paper was given by Chilow²⁾ and a review report by BITC.^{4), 5)}

The purpose of this study is to find the Hg content in workers' urine samples and compare the results with other investigations⁶⁾, and to develop a simple chemical separation of Hg after neutron irradiation of samples. In this work 45 samples were carefully collected from those who are working in various locations of two electrolysis plants using metallic mercury cells for about 8 h a day.

2. Experimental

2.1 Preparation of urine sample

All urine samples were collected in 100

ml polyethylene containers, and then added 50 mg K_2CrO_7 with 4 ml concentration HNO_3 to avoid the Hg absorption by container surface^{7), 8)}. The samples were kept in refrigerator.

2.2 Neutron activation

Pipet exactly 4 ml of urine sample which was then sealed in quartz tube. The Hg standard solution was prepared by dissolving metallic mercury (Merck, Germany) with nitric acid to make 10 $\mu g/ml$ solution. Each two samples and one standard were packed together in the rabbit and irradiated simultaneously. Neutron irradiation was carried out for 4 h in pneumatic tube of the THOR reactor of National Tsing Hua University which provided a thermal neutron flux about $2 \times 10^{12} n/cm^2 \cdot sec$.

2.3 Chemical separation

After cooling for 3 days, the irradiated samples and standards were transferred to a reflux system.⁹⁾ After adding 2 mg/ml Hg carrier, the sample was decomposed under reflux by adding continuously a mixture of HNO_3 and H_2O_2 until a clear solution was obtained, and then boiled to a small volume three times in order to expel any gaseous decomposition products. The solution was transferred to a 50 ml flask, which contained 500 mg of copper powder (30 mesh, Merck,

Germany). Then NaOH or HNO₃ was added to adjust the pH value. After shaking for 15 min, discard the upper layers solution, and the copper powder with Hg isotope was washed 5 times by using 1N HNO₃. The chemical yield by this procedure was 98.8~99.3%.

2.4 Counting and data processing

After the chemical separation, samples and standard were measured with a 4096-channel pulse height analyzer coupled to a Ge(Li) coaxial detector (ORTEC product), which gave a resolution of 2.8 keV (FWHM value) for the 1.33 MeV ⁶⁰Co photopeak. Two computer programs written in basic language for the HP 2116 MCA/basic system were designed to process the data. One was for system calibration and the other for calculation of the net areas under photo-peaks of the spectrum.

3. Results and Discussion

The quantity of copper powder, the pH value and the shaking time for the deposition of trace mercury are shown in Tables 1~3. The initial activities were 2.35×10^4 , 2.34×10^4 and 4.75×10^4 cpm/2 mg in 1 ml solution, respectively, and mixed with copper powder in nitric acid. The optimum quantity of copper powder is 400~500 mg (recovery 97.4~99.6%). The pH condition is on the higher acidity side and the efficient deposition

Table 1 The quantity of copper powder for the deposition of trace mercury

Cu powder (mg)	Radioactivity for deposition of Hg (cpm $\times 10^4$)	Deposition yield (%)
50	1.52	64.7
100	2.03	86.4
200	2.26	96.2
300	2.29	97.4
400	2.31	98.7
500	2.34	99.6
700	2.31	98.7
800	2.33	99.1

* The initial ²⁰³Hg activity was 2.35×10^4 cpm/2 mg in 1 ml solution.

Table 2 The pH value for the deposition of mercury on copper powder (500 mg)

pH value	Radioactivity for deposition of Hg (cpm $\times 10^4$)	Deposition yield (%)
5	3.56	74.9
4	4.05	85.2
3	4.40	92.6
2	4.65	97.8
1	4.72	99.3

* The initial ²⁰³Hg activity was 4.75×10^4 cpm/2 mg in 1 ml solution.

Table 3 The shaking time for the deposition of Hg on copper powder (500 mg)

Shaking time (min)	Radioactivity for deposition of Hg (cpm $\times 10^4$)	Deposition yield (%)
3	1.94	82.3
5	2.12	90.6
7	2.16	92.3
9	2.29	97.8
15	2.32	99.1
20	2.30	98.2

* The initial ²⁰³Hg radioactivity was 2.34×10^4 cpm/2 mg in 1 ml solution.

of mercury is attained at pH 1. The 10-min shaking time is sufficient to reach equilibrium for the deposition of Hg on copper powder.

In Tables 4 and 5, the results of the analysis of mercury contents in the workers urine of two plants are summarized. The concentration of Hg is the mean values of triplicate runs and the standard deviation was calculated in the usual manner. The mercury concentration in Factory A is smaller than that in Factory B. The current of Hg electrolysis cell in Factory A is lower, and the ventilation system in Factory A is better.

T. Gota and K. Matsunaga measured total Hg in air of the Hokkaido University with a mean value of 0.7~6.2 ng/m³ ¹⁰⁾. Janssen, et al. determined the mercury contents in work-room air of alkali chloride electrolysis plant equipped with mercury cells by atomic absorption method,¹¹⁾ and found that the Hg

Table 4 Mercury content in urine of the workers in the caustic soda production factory A

Sample No.	Working place	Hg content (ppb)	
			Mean value
A-1	Operator in electrolysis plant	40± 3.4	51.3± 4.2
A-2	"	45± 3.6	
A-3	"	33± 1.8	
A-4	"	87± 7.1	
A-5	Repairing man in electrolysis plant	133±13.4	146.5±14.2
A-6	"	160±15	
A-7	Washing man in electrolysis plant	130±12	119.5±11
A-8	"	121±12	
A-9	"	118±10	19 ± 1.5
A-10	Business office	22± 1.8	
A-11	"	16± 1.5	

concentration in air varied from 10 to 140 $\mu\text{g}/10\text{ m}^3$, which are much higher than Gota's results (normal place). The amount of Hg in workers' urine should be much higher than normal person whose mean value is 0.48~24.8 $\mu\text{g}/\text{liter}^6$.

Close examination of these two tables reveals that the contents of mercury in the urine of these workers depend very much on the working location inside the factory. The workers who are in charge of washing or repairing electrolysis cell have the highest mercury content in their urine in both plants.

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Table 5 Mercury content in urine of the workers in the caustic soda production factory B

Sample No.	Working place	Hg content (ppb)	
			Mean value
B-1	Repairing in electrolysis plant	250±20	341.7±23.4
B-2	"	150±13	
B-3	"	230±18	
B-4	"	340±28	
B-5	"	490±31	
B-6	"	590±30	
B-7	Operator in electrolysis plant	70± 7.2	142.8±13
B-8	"	270±23	
B-9	"	410±40	
B-10	"	80± 7.3	
B-11	"	130±11	
B-12	"	127±10	
B-13	"	140±13	
B-14	"	112±11	
B-15	"	90± 8	
B-16	"	260±23	
B-17	"	109±10	
B-18	"	43± 3.4	85.3± 8.3
B-19	"	24± 2.1	
B-20	"	134±13	
B-21	Operator in hydrochloric plant	34± 1.6	
B-22	"	24±13	
B-23	"	43± 3.8	
B-24	"	34± 1.6	
B-25	"	80± 7.4	
B-26	"	74± 6.8	
B-27	"	129±12	
B-28	"	120±11	
B-29	"	90± 8.8	27 ± 1.9
B-30	"	44± 4.0	
B-31	"	112±12	
B-32	"	140±30	
B-33	Business office	33± 2.1	
B-34	"	21± 1.8	

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要 旨

電解作業従事者の尿中の水銀の放射化分析

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塩化アルカリの水銀法電解プラントで働く作業員の尿につき、痕跡量の水銀を放射化分析法で定量した。照射後、水銀の化学的分離には、硝酸酸性溶液を銅粉末と振りまぜて、水銀を析出させるアマルガム析出法を用いた。分離条件を検討した結果、銅粉末の最適添加量は400～500 mg、溶液の pH は 1、振りまぜ時間は10min でよいことがわかった。45試料について得られた水銀含有量は33～600 ppb であり、その量は作業条件と密接な関係のあることが示された。