Note

Trace Elements in the Urine of Diabetics Determined by Instrumental Neutron Activation Analysis[†]

Tadashi ISHII, Kimiko HORIUCHI, Hiromichi NAKAHARA
and Yukio MURAKAMI

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University
Fukasawa 2-1, Setagaya-ku, Tokyo 158

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1. Introduction

Recently, much research has been carried out in an attempt to correlate the concentrations of trace elements in the body and various diseases¹⁾. Blood, serum and hairs are most commonly regarded as possible indicators of trace element variations within the body since they are easy to obtain and select. However, urine is also easy to obtain and can be another possible indicator especially for the patients suffering from kidney malfunction although it is very susceptible to diet.

In this work, trace-element analysis was performed on the urine samples of both the normal men and the patients diagnosed as diabetes in order to see if there were any correlations between the trace-element contents in urine and the disease. As it is desirable to determine as many elements as possible from the same sample, instrumental neutron activation analysis was employed.

2. Experimental

Samples Urine samples from thirty-four patients and seven normal men were analyzed. Since each sample had more or less residues, a few ml of conc. HNO₃ of analytical grade was added and stirred until the urine became seem-

ingly clear. Then, 10 ml of each sample solution was pipetted into a quartz evaporation dish and one ml of HNO₃ was further added. The dish was placed in a quartz tube in nitrogen atmosphere and heated gently from outside by infrared lamps. The heating was continued until the organic substance was almost completely ashed and slightly yellowish white residue was obtained. The total amount of the residue was weighed and about 50 mg was doubly sealed in polyethylene bags for neutron irradiation. As standards, GSJ JB-1 and JG-1 reference rocks (about 50mg each) were used for the determination of Na, Mg, Al, K, Sc, V, Fe, Co and Rb.

For Cl, Cr, Zn, Se, Br and Cs standard solutions of appropriate concentrations were prepared from the respective reagents of analytical grade and 50 μ l to 100 μ l were pipetted onto small pieces of filter paper and dried at room temperature.

Irradiation Neutron irradiations were carried out in the TRIGA MARK II Reactor of St. Pauls'. Three kinds of irradiation periods, 5 min, 6 hr, 24 hr, were chosen depending on the half-lives of the product nuclides. The neutron flux was in the range of 5.0×10^{11} to 1.2×10^{12} n/cm²·sec.

Activity measurement The gamma rays emitted from the product nuclides were measured by a 40 cc Ge(Li) detector connected to a 2048 channel pulse height analyser. The half lives and the gamma-ray energies used for the determination are shown in Table 1.

[†] 放射化分析による糖尿病患者の尿中の微量元素の定量. 石井 忠, 堀内公子, 中原弘道, 村上悠紀雄: 東京都立大学理学部化学教室, 158 東京都世田谷区深沢2-1-1

Table 1 The content in trace elements in human urine ($\mu\text{g/ml}$)

Element	Nuclide	Energy (keV)	$T_{1/2}$	Diabetes			Normal		
				range	average	σ	range	average	σ
Na	^{24}Na	1369	15 h	4662 -1173	2801	990	4289-920.9	2803	1228
Mg	^{27}Mg	1013	9.64m	130.5 -23.67	55.50	23.96	171.6-9.595	79.92	43.4
Al	^{28}Al	1780	2.31m	6.643 -0.368	3.174	1.650	10.64-1.898	5.270	2.847
Cl	^{38}Cl	1642	37.3m	152.5 -7.38	71.3	43.7	5213-48.5	1260.7	1594.6
K	^{42}K	1524	12.4 h	4350 -377.8	1422	933	1448-372.4	867.8	333.1
Sc	^{46}Sc	889	83.9 d	4.51-0.37 ($\times 10^{-4}$)	1.50 $\times 10^{-4}$	1.16 $\times 10^{-4}$	3.36-0.52 ($\times 10^{-4}$)	1.91 $\times 10^{-4}$	0.90 $\times 10^{-4}$
V	^{52}V	1434	3.75m	7.06-1.27 ($\times 10^{-2}$)	3.43 $\times 10^{-2}$	1.93 $\times 10^{-2}$	7.06- ($\times 10^{-2}$)*	5.47 $\times 10^{-2}$	0.25 $\times 10^{-2}$
Cr	^{51}Cr	320	27.8 d	1.80-0.35 ($\times 10^{-2}$)	0.99 $\times 10^{-2}$	0.42 $\times 10^{-2}$	4.96-1.42 ($\times 10^{-2}$)	2.67 $\times 10^{-2}$	1.43 $\times 10^{-2}$
Fe	^{59}Fe	1292	45.6 d	1.57-0.47	1.06	0.36	1.52-0.54	1.16	0.44
Co	^{60}Co	1332	5.263 y	4.77-1.30 ($\times 10^{-3}$)	2.62 $\times 10^{-3}$	0.97 $\times 10^{-3}$	1.68- ($\times 10^{-3}$)*	1.35 $\times 10^{-3}$	0.24 $\times 10^{-2}$
Zn	^{65}Zn	1115	245 d	14.6-0.11	1.87	3.54	1.69-0.42	0.88	0.28
Se	^{75}Se	265	120.4 d	6.91-0.90 ($\times 10^{-2}$)	3.22 $\times 10^{-2}$	1.74 $\times 10^{-2}$	47.9-4.35 ($\times 10^{-2}$)	16.03 $\times 10^{-2}$	14.91 $\times 10^{-2}$
Br	^{80}Br	618	17.6m	6.834-0.329	1.317	1.28	5.35-0.75	2.632	1.447
Rb	^{86}Rb	1078	18.66 d	5.19-0.30	1.76	1.32	1.75-0.94	1.33	0.27
Sb	^{124}Sb	720	60.4 d	1.04-0.36 ($\times 10^{-2}$)	0.77 $\times 10^{-2}$	0.29 $\times 10^{-2}$	25.6-5.07 ($\times 10^{-2}$)	14.9 $\times 10^{-2}$	8.40 $\times 10^{-2}$
Cs	^{134}Cs	796	2.046 y	13.1-0.52 ($\times 10^{-3}$)	5.07 $\times 10^{-3}$	2.99 $\times 10^{-3}$	9.53-3.43 ($\times 10^{-3}$)	6.67 $\times 10^{-3}$	2.23 $\times 10^{-3}$

* The minimum value was below the detection limit in this work, namely $1.0 \times 10^{-2} \mu\text{g/ml}$ for V, $1 \times 10^{-3} \mu\text{g/ml}$ for Co.

3. Results and Discussion

The results are summarized in Table 1 for 16 elements in terms of the concentration ranges and averages of 34 patients and 9 normal men. The standard deviations among the samples are also shown. The logarithms of the ratios of the elemental concentrations observed among the patients to those of the normal men are plotted in Fig. 1. The vertical lines with open circles show the ranges found among the normal men. From the figure it may be suggested that the chromium content in the urine of the diabetes patients is below normal as pointed out by Mertz²⁾, and that the selenium and cobalt contents are appreciably different from those of the normal men. In Fig. 2, is depicted how each elemental concentration varies among the individuals. The histograms are shown in terms of the percentage occurrence out of the total number of samples that could be analyzed in

the present work, namely, above the detection limit for the respective element.

The abscissa is taken in unit of $\log(\mu\text{g/g})$. The normal men are shown by shaded histograms while the diabetes patients, by open ones. Wide variation of the concentrations among the individuals is typical for the urine samples but is not usually observed for the blood or serum samples³⁾.

4. Conclusion

Urine samples from 34 diabetes patients and 9 normal men were analyzed by instrumental neutron activation analysis. It was found that the urine samples from the patients were rather deficient in chromium and selenium, and more abundant in cobalt. In order to make the conclusion more definite, it is suggested to analyze a larger number of samples taken from men on controlled diet.

Fig. 1 Histograms showing the spread in elemental concentration among various urine samples.

Fig. 2 Average concentrations of minor elements in urine observed among the diabetes patients shown in terms of $\log (\bar{x}_D/\bar{x}_N)$ where $\bar{x}_D$ and $\bar{x}_N$ denote the average value for patients and normal men, respectively.

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