SIMULTANEOUS DETERMINATION OF TRACE ELEMENTS IN URINE BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

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Abstract - Trace amounts of cadmium, chromium, nickel, and lead in urine were determined by simultaneous multielement graphite furnace atomic absorption spectrometry. Palladium chloride was employed as a matrix modifier. The urine was diluted 1+1 with distilled water, and introduced into simultaneous multielement atomic absorption spectrophotometer together with palladium solution. Standard addition methods were recommended for these elements analysis. Cadmium, chromium, nickel and lead contents determined by the proposed method ranged 0.2-2.4 μl , 1.0-3.0 μl , 0.2-4.8 μl , and 5.0-10.0 μl , respectively.

Keywords Urine, ultra trace elements, simultaneous multielement atomic absorption Spectrophotometry

Cadmium, chromium, nickel and lead are widely used in the various kinds of chemical industry. The fumes and dust of these metals and their compounds are very toxic and have been related to an increase in the incidence of cancer. Occupational exposure to cadmium, chromium, nickel and lead can be determined by means of workplace air measurements and biological monitoring. In biological monitoring, the cadmium, chromium, nickel and lead of the urine of the workers are measured [1]. In this study, we report on a method for the simultaneous determinations of cadmium, chromium, nickel and lead in urine. After a dilution of urine, palladium was employed as a matrix modifier and the cadmium, chromium, nickel and lead were measured by simultaneous multielement graphite furnace atomic absorption spectrophotometer (GFAAS).

EXPERIMENTAL

Apparatus A zeeman atomic absorption spectrometer (Hitachi Model Z-9000) equipped with pyro-cuvette (Hitachi 180-7444) was employed. The light sources were Hitachi hollow cathode lamp of cadmium, chromium, nickel and lead.

Reagents A matrix modifier was prepared by dissolving 17.7mg of palladium chloride in 100ml of hydrochloric acid(2%). Cadmium, chromium, nickel and lead standard solutions were prepared by combination of single element standards purchased from a commercial source(Wako Pure Chemical Industries, Ltd., 1000 ppm). All solutions were prepared from analytical reagent grade chemicals and distilled water, and stored in polyethylene bottles.

Procedure Urine was diluted 1+1 with distilled water. Twenty μl of the diluted urine was injected into the pyrolytically coated graphite tube together with 10 μl of 1 mg ml^{-1} palladium solution. The diluted urine was dried at 90-120 $^{\circ}\text{C}$ for 60 sec, ashed at 900 $^{\circ}\text{C}$ for 60 sec, and atomized at 2900 $^{\circ}\text{C}$ for 7 sec. using "optical temperature control" and "carrier gas interrupt" modes. Finally, pyrolytically coated graphite tube was cleaned at 3000 $^{\circ}\text{C}$ for 3 sec. The absorption signals of cadmium, chromium, nickel and lead were recorded at 228.8nm, 357.9nm, 232.0nm and 283.3nm, respectively.

RESULTS AND DISCUSSION

Selection of graphite tube and matrix modifier To set up the analytical conditions, a comparison was made among the sensitivities obtained with a pyrolytically coated tube, a graphite tub and a graphite cup. The sensitivity of pyrolytically coated tube in chromium and nickel analysis were

about 3.45 and 3.60 times as high as that of a graphite tube and a cup, respectively. Next, in order to select for a more suitable matrix modifier for the simultaneous determination of analyte metals, the stabilizing effects of copper, palladium and rhodium were compared. Among these matrix modifiers, palladium was the best for these elements sensitivities of all in diluted urine. In the presence of palladium, the atomic absorption signals of lead and nickel were improved by 70% and 40%, respectively.

Furnace parameters The peak heights obtained for diluted urine of cadmium, chromium, nickel and lead were shown in Fig. 1 as a function of ashing and atomization temperatures. The temperature in the ashing stage greatly affects cadmium, and lead atomization. With an ashing temperature above 1000 °C and 1200 °C for 60 s, the signal of cadmium and lead were lowered. At the atomization stage, the cadmium, chromium, nickel and lead peak heights were maximum and constant over the tested temperature range of 2900–3000 °C for 10 s of heating.

Fig. 1 Thermal pretreatment and atomization curves for cadmium, chromium, nickel and lead with the palladium chlorides modifier in urine matrices. —●—, Cd ; -●-, Cr ; —○—, Ni ; -○--, Pb.

Effects of foreign ions The effects of foreign ions on the graphite furnace atomization of cadmium, chromium, nickel and lead were studied. Many ions, e.g., Ca, Cl⁻, etc. gave negative errors of 11–85% when they coexisted with cadmium, chromium, nickel and lead at the levels found in the urine sample.

TABLE 1 Interference effects on determination of cadmium chromium nickel and lead in the presence of palladium

Interferent	Conc. of matrices (mg ml ⁻¹)	Present in urine (mg ml ⁻¹)	Relative absorbance of elements			
			Cd	Cr	Ni	Pb
None			1.00	1.00	1.00	1.00
K ⁺	1.0	0.75	1.00	0.95	1.08	0.71
Na ⁺	5.0	1.31	0.98	0.96	0.89	0.83
Ca ²⁺	1.0	0.053	0.46	0.70	0.81	0.19
Mg ²⁺	0.05	0.032	0.38	0.96	1.06	1.06
Al ³⁺	1.0	0.000009	0.91	1.02	1.10	0.98
Cl ⁻	20.0	2.2	0.77	0.65	0.80	0.70
SO ₄ ²⁻	0.25	0.65	0.18	0.15	0.95	0.54

Accuracy of GFAAS in urinary trace elements analysis To check the accuracy of a direct determination of cadmium, chromium, nickel and lead in urine by GFAAS, the comparison between the standard addition method and the calibration curve method was studied. As shown in Fig. 2, the slopes of the standard addition plots differed from these of the calibration curves. Standard addition method was applied to ten normal urine samples and we knew similar depression relative to the aqueous curve shown in Fig. 2. Therefore, standard addition method was recommended for the determination of cadmium, chromium, nickel and lead in urine.

Fig. 2 Determination of trace elements in urine by graphite furnace atomic absorption spectrometry. A ○, aqueous calibration curve; B, C, D ●, standard additions of Cd, Cr, Ni and Pb to urine samples.

Detection limits The limits of detection were 0.2ppb for cadmium, 0.7ppb for chromium, 0.2ppb for nickel, and 2.0ppb for lead, defined as twice the standard deviations of the procedural blank signals ($n=3$). It can be seen that "normal" level in urine of cadmium, nickel and lead should be detectable; however, the detection limit of chromium is insufficient for "normal" levels in urine.

Results of analysis The analytical results for cadmium, chromium, nickel and lead in standard reference materials and 15 urine samples are summarized in Table 2. The results for cadmium, nickel and lead in the reference material agreed with its certified values. In 15 healthy non exposed subjects, the mean analytical values of cadmium, chromium, nickel and lead were 1.2, 1.5, 1.9 and 7.3 $\mu\text{g/l}$, respectively. The measured values for cadmium, nickel and lead were reasonable, although the concentrations of chromium were slightly high probably because of the contamination in the preparation stage.

Table 2 Analytical results of cadmium, chromium, nickel and lead in urine and standard reference materials.

Sample	Concentration, $\mu\text{g/l}$			
	Cd	Cr	Ni	Pb
Lanonorm metals*	-	4.1	2.9	11.0
Urine control**	5.4	7.2		57.0
normal*** persons	1.2 (0.2-2.4)	1.5 (1.0-3.0)	1.9 (0.2-4.8)	7.3 (5.0-10.0)

* Certified values of cadmium, chromium, nickel and lead are $117 \pm 17 \mu\text{g/l}$, $2.8 \pm 0.7 \mu\text{g/l}$, $3.0 \pm 0.6 \mu\text{g/l}$ and $10.0 \pm 1.5 \mu\text{g/l}$, respectively.

** Certified values of cadmium, chromium, and lead are $6.5 \pm 1.3 \mu\text{g/l}$, $5.9 \pm 1.2 \mu\text{g/l}$, and $52 \pm 9 \mu\text{g/l}$, respectively.

***Average values with ranges in parentheses in 15 subjects.

In conclusion, simultaneous multielemental analysis of trace elements in urine were achieved by GFAAS. In the proposed method, most of foreign ions and salts, which are highly concentrated in urine were removed by ashing stage using palladium modifier. By using the proposed method, less than 0.5 ml of urine was enough for the simultaneous analysis of cadmium, chromium, nickel and lead in healthy unexposed subjects.

REFERENCE

1. I.L.O., "Encyclopaedia of Occupational Health and Safety", Vol.II, p.765, International Labor Office, Geneva (1972).