Determination of Tellurium in Urine by Graphite Furnace Atomic Absorption Spectrometry after Solvent Extraction

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Trace amounts of tellurium in urine were determined by atomic absorption spectrometry using a graphite furnace atomizer. The urine was concentrated and digested with $\text{HNO}_3\text{--HClO}_4$. The bulk of salts and interfering elements were removed by 4-methyl-2-pentanone extraction procedure, and finally the organic phase was analyzed on a graphite furnace atomic absorption spectrometer equipped with an auto sampler having a concentration function. Recoveries of tellurium added to urine sample range from 90 to 103%; relative standard deviation was 9% at the 0.1 $\mu\text{g/l}$ level. Tellurium contents in urine ranged from <0.1 to 1.2 $\mu\text{g/l}$.

Keywords Tellurium, urine, solvent extraction, graphite furnace atomic absorption spectrometry

Tellurium is a member of the group VIb elements in the Periodic Table, to which selenium and sulfur also belong. Due to its photoelectric properties, Te and its compounds are widely employed in the semiconductor industry and electronics. In metallurgy, Te is employed as an additive to improve alloys.

Tellurium compounds are very toxic and affect various organs in ways similar to selenium ones. Nevertheless, Te has not caused serious social problem because of its low abundance in the environment. However, it is well known that men exposed to Te fumes and TeO_2 powder appear to suffer more severe peptic symptoms than men who were not working with Te compounds.¹

Because of their low sensitivities, the determinations of Te by the colorimetric method using Bismuthol II^{2,3}, by flame atomization atomic absorption spectrometry⁴ or by conventional graphite furnace atomic absorption spectrometry⁵ are not suitable for urine sample analysis. On the other hand, the graphite furnace atomic absorption spectrophotometer, which has a concentration function because sample injection and drying are repeated, has sufficient sensitivity for urine analysis. However, the study of interferences shows a significant suppressive effect upon the determination of Te by several foreign elements, *e.g.*, lead, copper and nickel, which are also concentrated in urine samples.

In this study, we report on a method for the determination of Te in urine. After a wet digestion of urine, the Te is isolated from foreign elements by solvent extraction, and measured on a graphite furnace atomic absorption spectrophotometer equipped with an autosampler having a concentration function.

Experimental

Reagents and apparatus

A matrix modifier was prepared by dissolving 17.7 mg of PdCl_2 in 100 ml of hydrochloric acid (2%). A Te standard solution was 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.

A Zeeman atomic absorption spectrometer (Hitachi Model Z-9000) equipped with pyro-cuvette (Hitachi 180-7444) was employed. The light source was a Hitachi hollow cathode lamp of Te.

Procedure

An urine sample of 50 ml was placed in a 200 ml conical beaker and digested with 20 ml of nitric acid and 3 ml of perchloric acid. After the digestion, the sample solution was evaporated to dryness on a hot plate at 230°C. One milliliter of hydrochloric acid was added to the residue and evaporated to dryness. The residue was taken up in 10 ml of 7 M hydrochloric acid. The sample solution was transferred to a test tube. The test tube was shaken for 30 s with 2–5 ml of MIBK (4-methyl-2-pentanone), and left standing for 20 min in order to separate the organic phase. Then 200 μl of the organic phase was transferred to a pyrocoated graphite tube by using the autosampler that had a concentration function. The sample solution was dried at 95–120°C for 120 s, and ashed at 1000°C for 180 s and atomized at 2400°C for 5 s. The absorption signal was recorded at 214.3 nm wavelength using a 0.9 nm slit width.

Results and Discussion

Furnace parameters

To set up the analytical conditions, several attempts were made. The best results were obtained by using a pyrocoated graphite tube and modifying the matrix with PdCl_2 . The effect of the modifier may be ascribed to the formation of relatively non-volatile Pd-Te compound in the graphite tube. These conditions enhanced the signal about twice. The absorbances obtained for organic extracts of Te are shown in Fig. 1, as a function of ashing and atomization temperatures. The temperature in the ashing stage greatly affects Te atomization. With an ashing temperature above 1000°C for 150 s, the signal was lowered. This means that a considerable amount of Te is volatilized before the atomization stage. At the atomization stage, the Te absorbance was maximum and constant over the tested temperature ranged of $2300\text{--}3000^\circ\text{C}$ for 5 s of heating. From these results, an ashing temperature of 1000°C for 180 s and an atomization temperature of 2400°C were selected for Te analysis.

Fig. 1 Effects of the ashing and atomization temperatures on the absorbance of Te in the presence and absence of matrix modifiers. O, 1.0 ng Te in 10 μg Pd; ●, 1.0 ng Te; atomization for curve O●, 2500°C ; ashing for curve O, 1000°C .

Fig. 2 Effect of acidity on the extraction of Te(IV) and Te(VI). O, Te(IV); ●, Te(VI); aqueous phase, 10 ml; organic phase, 4 ml; Te(IV), Te(VI), 0.2 μg .

Separation and concentration of tellurium

The applicability of the direct graphite furnace atomic absorption method reduces the absolute sensitivity of Te determination in urine. In fact, with the 1+1 dilution used in the procedure, it was not easy to analyze urine samples having an Te concentration below $10\text{ }\mu\text{g/l}$. In addition to this, when more than $60\text{ }\mu\text{l}$ of urine was injected into the pyrocoated graphite tube by the autosampler, the background absorbance was over 1.5 and could not be corrected by Zeeman effects. In contrast, with the wet digestion of 50 ml of urine and MIBK extraction from hydrochloric acid medium was applicable to urine samples with Te concentration down to $0.06\text{ }\mu\text{g/l}$ and lowered the background absorbance below 1.0. For this reason, the determination of Te by graphite furnace atomic absorption was also performed after acid digestion and MIBK extraction. The extraction behavior of Te(IV) and Te(VI) in MIBK was investigated. As shown in Fig. 2, the Te(IV) in urine matrices was extracted into MIBK in hydrochloric acid medium in the molarity range 7–8, whereas Te(VI) was not. The following procedure for quantitative separation from foreign ions is proposed: After reduction of the Te(VI) to Te(IV) by hydrochloric acid during drying cycle, the residue should be dissolved in 7 M hydrochloric acid. The sample solution should be shaken with MIBK and then the organic phase can be introduced into the atomic absorption spectrometer.

Reduction of tellurium(VI)

After wet digestion of urine, Te was present in the hexavalent state and could not be extracted into MIBK. Consequently, the actual analytical process, Te(VI) in sample solution must be reduced to Te(IV). Therefore, the reduction of Te(VI) to Te(IV) by hydrochloric acid during the drying cycle was studied. Our results indicate that 1 ml of hydrochloric acid was enough to reduce Te(VI); then further addition of hydrochloric acid tended to decrease the recovery of Te.

Effects of foreign ions

The effects of foreign ions on the graphite furnace atomization of Te were studied. The concentrations of foreign ions in this study were comparable to those that may be found in the urine used in the procedure. Table 1 compares the results obtained when $1\text{ }\mu\text{g}$ of Te(IV) was spiked with various foreign ions and then determined by atomic absorption spectrometry with and without solvent extraction. No interference was observed when many species, e.g., Mg^{2+} , Zn^{2+} , Al^{3+} , etc. were added to levels of $1000\text{ }\mu\text{g}$. Other ions, e.g., Ca^{2+} , Ni^{2+} and Cu^{2+} , etc. gave errors of 16–42% when they coexisted with Te at the levels found in the urine sample. Thus, the sample solution was extracted with MIBK to eliminate the effects of interfering cations and salts. As shown in Table 1, the proposed separation method reduced interference from most of foreign ions to $<10\%$.

Table 1 Effects of foreign ions on tellurium determination

Ion added	Amount added/ μg	Te found/ μg	
		Proposed method	Without separation
Na(I)	5000	0.92	0.90
Ca(II)	5000	0.95	1.42
Fe(III)	500	1.21	1.16
Cu(II)	500	1.06	0.76
As(III)	500	0.92	0.93
Se(IV)	500	0.98	0.92
Cd(II)	100	1.02	1.05
Ni(II)	500	0.94	0.65
Pb(II)	500	1.01	0.85

One microgram of Te was taken. The following ions do not interfere in excess amount (1000 μg): Be(II), Al(III), Ti(II), Mg(II) and Zn(II).

Table 2 Recovery of tellurium added to urine sample by proposed method

No.	Sample taken/ml	Te/ μg		Recovery, %
		Added	Found	
1	30	0	0.00	—
2	30	0.1	0.09	90
3	30	0.2	0.19	95
4	30	1.0	1.03	103
5	50	0.2	0.18	90

Sensitivity and lower limit of detection

The sensitivity of Te in the final sample solution by this method was 0.4 ppb. The limit of detection was 0.005 μg for Te, defined as twice the standard deviations of the procedural blanks ($n=3$).

Recovery test

In order to investigate the applicability of the proposed method to urine samples, the recovery of known amounts of Te added to urine samples was examined. The amounts of Te added were 0.1, 0.2 and 1.0 μg . The results shown in Table 2 indicate that the Te recoveries ranged from 90 to 103%, and the relative standard deviation (five replicate samples) is about 9% at the 0.1 μg level.

Table 3 Analytical results for tellurium in urine sample by proposed method

No.	Sample taken/ml	Te found/ μg	Te content/ $\mu\text{g/l}$
1	30	0.016	0.5
2	30	0.028	0.9
3	30	<0.005	<0.2
4	50	<0.005	<0.1
5	50	<0.005	<0.1
6	50	<0.005	<0.1
7	50	0.06	1.2
8	50	<0.005	<0.1
9	50	0.04	0.8
10	50	<0.005	<0.1

Results of the analysis

The analytical results for Te in ten urine samples are summarized in Table 3. In ten healthy non-exposed subjects, the concentrations of Te in urine ranged from <0.1–1.2 $\mu\text{g/l}$, averaging 0.4 $\mu\text{g/l}$. These values were about two orders of magnitude below that of selenium, which also belongs to group VI elements. The agreement between the method proposed here and the hydride generation method was checked and found to be within the usual limits of variation for elemental analysis.

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(Received July 27, 1989)
(Accepted October 23, 1989)