Determination of Tin in Biological Samples by Gaseous Hydride Generation-Atomic Absorption Spectrometry

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SUMMARY

A highly sensitive tin determination method for biological samples is presented. Tin reduced to gaseous hydride by sodium tetrahydroborate solution and trichloroacetic acid solution was atomized through an electrically heated silica tube and measured by atomic absorption spectrometry at a wavelength of 286.3 nm. Sample decomposition procedure was avoided in determining tin in urine in order to avoid contamination with tin tin acids used for sample digestion. Recovery of tin was 80% at 1:5 dilution of human urine and was 102% at 1:10 dilution. The relative detection limit of urine tin was 2.0 ng/ml, that of standard tin solution was 0.3 ng/ml and urine was diluted 5-fold to determine tin concentration. A 10 ml sample solution is necessary for determining of tin. The coefficient of variation of human urine tin determination was 1.6% at 10 ng/ml. The method can be applied to determination of tin concentration in biological samples.

INTRODUCTION

It has been suggested that tin is an essential trace element[1] and exists in small amount in biological materials[2-3]. A very simple and sensitive method is required to measure tin concentration in biological materials for investigation of nutritional state of tin. We report, herein, a determination method for tin in biological samples (human and rat urine) and canned food using gaseous hydride generation-atomic absorption spectrometry (GHG-AAS)[1-7] with an electrically heated silica tube. Since tin content of the NBS standard reference material is not certified by the National Bureau of Standards, the tin concentration in the syrup of canned pineapple was determined by GHG-ASS and flame-AAS for reference.

MATERIALS AND METHOD

Materials

Human urine samples were collected from nine healthy adult males (23–25 years old) at random times. Rat urine samples were obtained from four adult male Wistar rats. Canned pineapple syrup was sampled immediateley after opening the can.

Apparatus

Nippon Jarrell-Ash AA-782 atomic absorption spectrophotometer was used for GHG-AAS. Shimadzu Model AA-670 atomic absorption spectrophotometer was used for flame-AAS. Hamamatsu Photonics tin hollow cathode lamp was used at wavelength 286.3 nm with 10 mA lamp current. Nippon Jarrell-Ash Hydride Generator HYD-1 was used for generation of tin

hydride. Nippon Jarrell-Ash HYD-2 was used for atomizing tin by heated silica tube.

Reagent

Trichloroacetic acid (TCA) and sodium tetrahydroborate ($NaBH_4$) were used for generation of hydride. Tin (Ⅳ) standard solution was prepared from anhydrous tin (Ⅳ) chloride. Tin (Ⅱ) standard solution and other standard solutions of metals were prepared from commercially available reagent for atomic absorption spectrometry. Nitric acid (co. 60%) and perchloric acid (co. 60%) were used for sample decomposition. Hydrochloric acid (co. 30%) and oxalic acid were compared with trichloroacetic acid for generation of hydride. All reagents were the best grade obtained from Wako Pure Chemicals Industries, LTD.

Pretreatment of samples

Canned pineapple syrup (5ml) was added in a 100ml Kjeldahl flask containing 10ml nitric acid (co. 60%) and 5ml perchloric acid (co. 60%). The mixture was heated for 20 minutes until white fumes appeared. The solution was further diluted with double-distilled water (DDS) and added to an adequate volume of TCA. No decomposition procedure for urine samples was employed. Samples were diluted with DDS and added to TCA to bring the final concentration of TCA to 2%.

RESULTS AND DISCUSSION

Analytical conditions of HYD-1.

Analytical conditions of HYD-1 are shown in Fig.1.

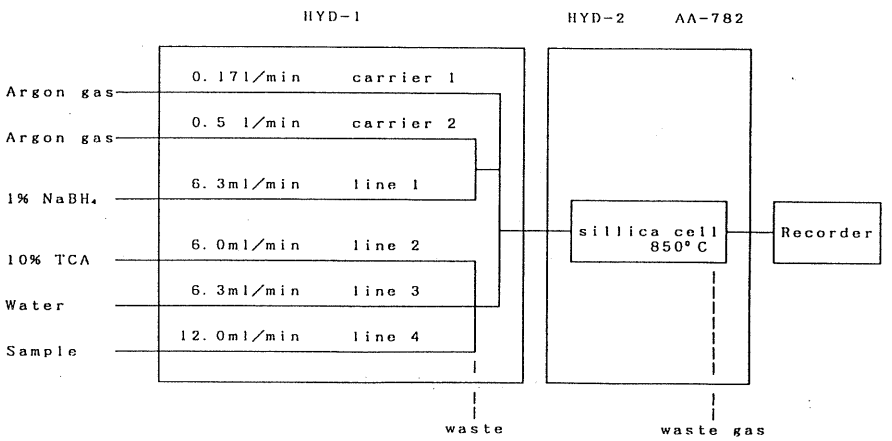

Fig. 1. System diagram for tin determination.

Sodium tetrahydroborate solution (line 1): This solution must be freshly prepared from powder for each analysis.

Acid solution (line 2): The sensitivity of GHG-AAS for tin has been reported to be strongly dependent on the kinds and concentration of acids[4-7]. To determine an acid suitable for generation of the hydride, we examined hydrochloric acid, TCA and oxalic acid. When hydrochloric acid was used in place of TCA, the sensitivity was reduced. Oxalic acid was ineffective in generating hydride.

Sample (line 4): The effect of acid concentration in the sample is shown in Fig.2. Though both

TCA and hydrochloric acid gave the same maximum response, TCA gave a broad maximum over the range of concentration of 1.6–5% (w/v) as compared with a narrow maximum of hydrochloric acid at a concentration of about 0.05% (w/v). TCA was practical for determination. A 10ml sample solution was necessary for determination.

Condition of the silica tube.

Temperatures of the silica tube between 700–1000°C were examined. A temperature of 850°C was considered optimal.

Precision and accuracy.

The calibration curve for tin (Ⅱ) standard solution is shown in Fig.3. The curve was linear up to 10ng/ml tin. The precision was estimated from 5 times determination of a 5 ng/ml tin standard solution. The coefficient of variation was 2.4%. The relative detection limit corresponding to twice the standard deviation of the base line noise was 0.3ng/ml. Tin (Ⅱ) was used for tin standard in further investigation because tin (Ⅱ) and tin (Ⅳ) responded identically in this study.

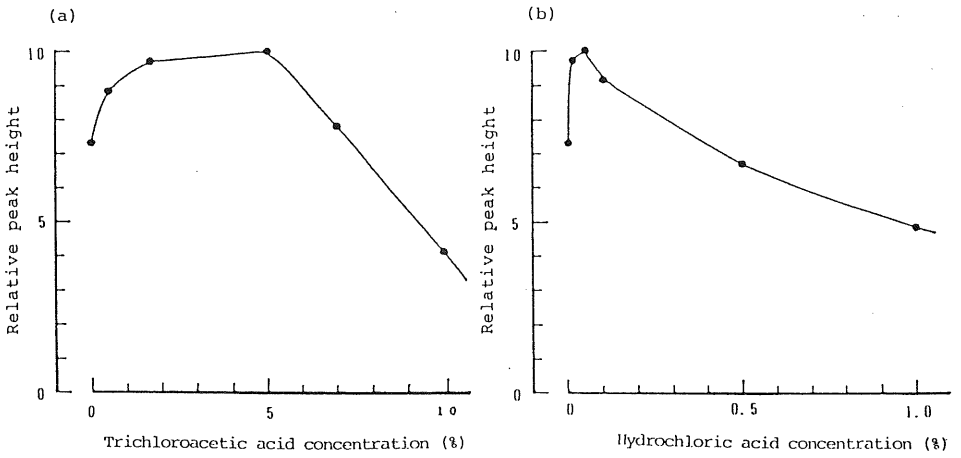

Fig .2. Effects of acid concentration in sample tin (Ⅱ) solution on sensitivity.

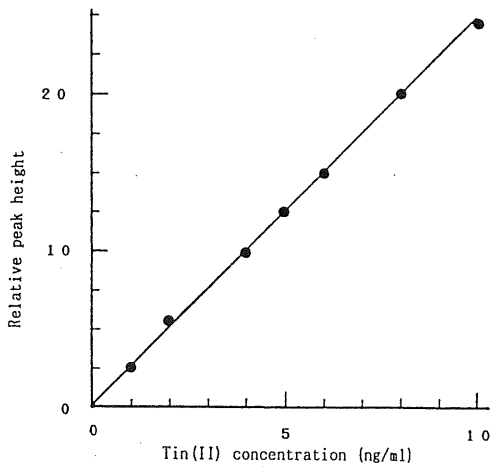

Fig .3. Calibration curve for tin (Ⅱ) standard solution.

Interferences

The possible effects of other elements existing in biological samples on determination are shown in Table 1. Nickel and selenium interfere severely. As their concentrations in biological samples are low in general, their interference is negligible in the determination of tin in biological samples.

Table 1. Influence of coexistent elements on determination of tin(II) 5 ng/ml in 0.05 %(w/v) HCL solution

Coexistent element	Conc. (ng/ml)	Recovery (percent change in response)
Na(I)	800,000	− 8
	50,000	0
K(I)	600,000	− 4
	50,000	0
Ni(II)	1,000	−53
	500	−35
	100	0
Cu(II)	14,000	−46
	7,000	−23
	1,400	− 5
Fe(III)	50,000	−14
	10,000	− 8
	5,000	0
Co(II)	10,000	− 8
	1,000	− 3
	100	0
Se(IV)	200	−51
	100	−17
	50	− 3
Ge(IV)	12,500	−55
	5,000	−33
	2,500	0
As(III)	50	−25
	30	0

Determination of tin in urine

The effect of dilution volumes on tin determination is shown in Table 2. The standard addition technique was used to avoid interference. The detection limit of urine tin was 2.0ng/ml, as the detection limit of tin standard solution was 0.3ng/ml and recovery was 79.5% at 5-fold dilution of human urine. The coefficient of variation of human urine analysis was 1.6% at 10ng/ml (3 determinations). Result of determination of urine is shown in Table 3.

Determination of the syrup

Canned pineapple syrup, which contains a high concentration of tin, was analyzed by GHG-AAS and flame-AAS using air-acetylene flame. Results are shown in Table 4. Both the techniques yielded almost same value. Recovery of tin in digestion was 103%.

Table 2. Effect of dilution on determination of urine tin by GHG-AAS

Sample	Dilution	Recovery
Human urine	1:2	46%
	1:5	80%
	1:10	102%
Rat urine	1:400	83%
	1:500	96%

Table 3. Determination of tin in urine samples by GHG-AAS

Sample	Tin concentration (ng/ml)				
Human urine	<2.0,	<2.0,	2.0,	4.5,	5.0,
	6.4,	7.6,	9.0,	11.0	
mean ± S. E.*	5.1 ± 1.3				
Rat urine	11.0,	26.0,	54.0,	150.0	

* : <2.0 is considered as 0.

Table 4. Determination of tin in five samples obtained from the syrup of the same pineapple can by GHG-AAS* and flame-AAS

	GHG-AAS*	Flame-AAS
Mean (μg/ml)	69.7	70.1
S. D. (μg/ml)	2.9	3.3
C. V. #	4.2	4.8

*: Gaseous hydride generation-atomic absorption spectrometry

#: Coefficient of variation.

REFERENCES

1. Schwarz, K., Milne, D. B. and Vinyard, E. (1970): Growth effects of tin compounds in rats maintained in a trace element-controlled environment. Biochem. Biophys. Comm., 40, 22–29.
2. Schroeder, H. A., Balassa, J. J. and Tipton, I. H. (1964): Abnormal trace metals in man:Tin. J. Chron. Dis., 17, 483–502.
3. Weber, G. (1985): Bestimmung von Zinnspuren in wäßrigen Matrices mit Voltammetrie und Atomabsorptionsspektrometrie. Fresenius Z. Anal. Chem., 322, 311–322.
4. Vijan, P. N. and Chan, C. Y. (1976): Determination of tin by gas phase atomization and atomic absorption spectrometry. Anal. Chem., 48, 1788–1792.
5. Evans, W. H., Jackson, F. J. and Dellar, D. (1979): Evaluation of a method for determination of total antimony, arsenic and tin in foodstuffs using the hydride generation technique. Analyst, 104, 16–34.
6. Chan, C. Y. and Baig, M. W. A. (1982): Semi-automatic method for determination of total tin in rocks. Anal. Chim. Acta, 136, 413–419.
7. Maher, W. (1982): Measurement of total tin in marine organisms by stannane generation and atomic absorption spectrometry. Anal. Chim. Acta, 138, 365–370.