Determination of tin in geological materials by atomic absorption spectrometry

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Abstract: A rapid and sensitive method for the determination of tin in geological materials by atomic absorption spectrometry using either the combination of hydride generation and heated quartz cell atomizer or solvent extraction and carbon tube atomizer was investigated. Common silicate rocks and sediments were decomposed with a mixture of perchloric, nitric and hydrofluoric acids, and dissolved in diluted hydrochloric acid and oxalic acid solution. Tin hydride was generated with 1% sodium tetrahydroborate and 0.6M hydrochloric acid using an automated hydride generator, and introduced to a quartz cell atomizer.

The combination of solvent extraction and carbon tube atomizer was adopted for samples containing a large amount of interfering elements and/or refractory tin-bearing minerals. In this case the samples were decomposed by the acid mixture or fusion with sodium carbonate and boric acid. Tin was extracted by butyl acetate as tin-trioctylphosphine oxide (TOPO) complex from 2.4M hydrochloric acid solution containing 40 mg of aluminium as chloride. The tin in the organic solvent was determined by a carbon tube atomizer.

The limit of detection in the determination of tin is 0.1 ppm by hydride generation and quartz cell atomizer, and 0.04 ppm by solvent extraction and carbon tube atomizer for 0.5 g of a given sample. The reletive standard deviation for the determination of more than 0.5 ppm tin was less than 14%. The method can be satisfactorily applied to the analysis of a great variety of geological reference samples.

1. Introduction

The analytical method for the determination of tin by atomic absorption spectrometry using an argon-hydrogen flame after extraction of tin(IV) as iodide with benzen have been previously reported (TERASHIMA, 1975 and 1982). However, the analytical procedures are rather complicated, and the sensitivity is not high enough for applying it to geological materials containing a trace amount of tin in 0.2 ppm level.

Recently, a convenient and useful apparatus which consists of an automated, continuous hydride generator and an electrically heated quartz cell atomizer has been developed (SUBRAMANIAN and SASTRI, 1980; IKEDA *et al.*,

1981a, b; CHAN and BAIG, 1982). This apparatus provides high sensitivity and rapid analysis. Although the combination of hydride generation and quartz cell atomizer can be usefully applied to common geological samples, some minerals which contain a large amount of interfering elements and refractory tin-bearing minerals can not be safely analysed by this method. For such minerals, ZHOU *et al.* (1984) have studied the method which uses a carbon tube atomizer with solvent extraction. In the present study, these two different procedures for tin analysis were evaluated and modified after detailed examination concerning the effect of concomitant elements and the dissolution or digestion methods for a great variety of geological materials.

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2. Experimental

2. 1 Apparatus

The Nippon Jarrell-Ash Model AA-781 atomic absorption spectrometer used was equipped with a Nippon Jarrell-Ash Model HYD-1 automated hydride generator, a Model HYD-2 heated quartz cell atomizer, a Model FLA-10 carbon tube atomizer unit, a deuterium background corrector, and a tin hollow-cathode lamp (Hamamatsu Photonics).

A shematic diagram of the HYD-1 automated hydride generator can be seen in Fig. 1. A peristaltic pump and controller were used to mix sample with hydrochloric acid and then with sodium tetrahydroborate solution. In a water-cooled reaction coil gaseous tin hydride was produced and the hydride was introduced by argon carrier gas into a quartz cell atomizer (HYD-2) after passing through the first gas-liquid separator, condenser, second gas-liquid separator and buffer tank. The temperature of the quartz cell atomizer (140 mm long, 11 mm i.d.) was controlled at $900\pm20\,^{\circ}\mathrm{C}$ by a variable transformer.

For use of a carbon tube atomizer for tin determination, it has been reported that the impregnation of the carbon tube with tungstate solution rises the analytical sensitivity nearly two times, and also improves the precision of the absorbance readings (ZHOU et al., 1984). Because the evidences reported were confirmed in this study, the carbon tubes were soaked overnight in a 8% solution of sodium tungstate dihydrate, and dried at $120\,^{\circ}\mathrm{C}$ in an electric oven for about 4 hours.

2. 2 Reagents

Tin standard solutions (0.01, 0.05, 0.5 and 10 μg/ml): Prepare by consecutive dilution of a 1 mg/ml atomic absorption standard with 0.6M hydrochloric acid.

Sodium tetrahydroborate solution (1%): Dissolve 10 g of sodium tetrahydroborate in 1000 ml water with 5 g of sodium hydroxide.

Oxalic acid solution (10%): Dissolve 50 g of oxalic acid in water and dilute to 500 ml.

Aluminium chloride solution (Al 20 mg/ml): Dissolve 49.4 g of aluminium chloride in water
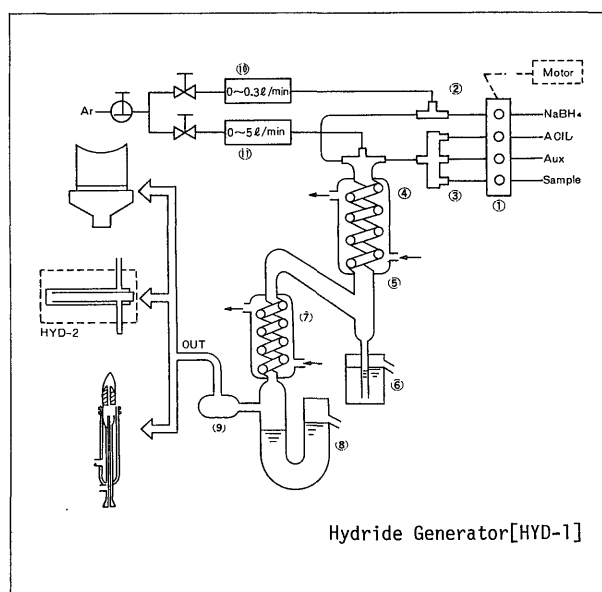

Hydride Generator[HYD-1]

Fig. 1   Schematic diagram of the hydride generator (Nippon Jarrell-Ash, Model HYD-1). ① Peristaltic pump and controller   ② Gas-liquid joint   ③ Manifold   ④ Water-cooled reaction coil   ⑤ First gas-liquid separator   ⑥ Waste water bottle   ⑦ Condenser   ⑧ Second gas-liquid separator   ⑨ Buffer tank   ⑩ Flow meter for carrier I   ⑪ Flow meter for carrier II.

and dilute to 500 ml.

Ascorbic acid solution (10%): Dissolve 20 g of ascorbic acid in water and dilute to 200 ml (prepare flesh daily).

TOPO(trioctylphosphine oxide)-Butyl acetate solution: Dissolve 8 g of TOPO in 200 ml of n-butyl acetate.

All other reagents were of anlaytical reagent grade.

2. 3 Recommended procedures for hydride generation and quartz cell atomizer

Acid digestion for common geological meterials: Weigh accurately 0.1 to 0.2 g of powdered sample into a Teflon beaker. Add 3 ml of 60% perchloric acid, 3 ml of concentrated nitric acid and 5 ml of 46% hydrofluoric acid, and mix them. After letting the mixture stand for 15–20 min, evaporate the mixture to dryness on a sand bath at about 220 °C. Add 1 ml of 3M hydrochloric acid, and heat until a yellow colour of iron (III) is obtained; then add 5 ml of 10% oxalic acid, and heat for 3–5 min. After cooling, transfer whole solution (if the content of tin is less than 5 μg) or a portion of the solution to a 25 ml volumetric flask. Adjust the final acidity to about 0.12M

Table 1   Operating conditions for tin determination.

Wavelength	224.6 or 254.7 nm
Lamp current	10 mA
(Hydride generator, HYD–1)	
Sample solution, feed rate	20 ml/min
NaBH$_4$ solution, feed rate	12 ml/min
concentration	1% in 0.5% NaOH
HCl solution, feed rate	12 ml/min
concentration	0.6M
Argon flow, carrier I	0.1 l/min
carrier II	1.0 l/min
(Hydride atomizer, HYD–2)	
Temperature	900±20 °C
(Carbon tube atomizer, FLA–10)	
Drying	30 A–20 sec.
Charring	100 A–30 sec.
Atomizing	200 A–7 sec.
Lamp mode	2
Argon flow rate	2 l/min

for hydrochloric acid concentration and 5% for oxalic acid, and add 2.5 ml of aluminium chloride solution (Al 20 mg/ml), then make up exactly to 25 ml with water.

Introduce the solution into the hydride generator for 30–40 s, and determine tin under the operating conditions given in Table 1. Calculate the tin concentration directry from a calibration graph based on peak heights obtained by taking 0–5 μg of tin in 25 ml volumetric flasks, and proceeding as described above.

2. 4 Recommended procedures for solvent extraction and carbon tube atomizer

Acid digestion for common geological materials: Decompose 0.1 to 0.5 g of sample by the acids as mentioned above. Dissolve the residue by heating with 8 ml of hydrochloric acid (1+1). Transfer the solution to a 50 ml separatory funnel. Add 2 ml of aluminium chloride solution, and dilute to about 18 ml with water. Add 3 ml of 10% ascorbic acid solution, and mix. Shake with 5 ml of TOPO-butyl acetate for 3 min. Determine the tin absorbance of 20 μl of the organic layer with a carbon tube atomizer under the operating conditions listed in Table 1. If the content of tin in organic phase is more than 5 μg, determination of tin by a nitrous oxide-acetylene flame is recommended. Prepare a calibration curve by adding 0–50 μg of tin to 8 ml of hydrochloric acid (1+1) in separatory funnels, and proceed as described above.

Sodium carbonate and boric acid fusion for refractory geological materials: Weigh 0.05 to 0.1 g of powdered sample into a platinum crucible. If the samples contain more than 1% of noncarbonate carbon, pre-heat the samples at about 600 °C to remove this carbon. Add 1 g of sodium carbonate and 0.2 g of boric acid, and mix them. Fuse the mixture cautiously over a Meker burner for the first 2–3 min to minimize spatter. Cover the crucible, and transfer it into an electric furnace at about 1000 °C for 5–30 min. After cooling, dissolve the melt by heating with 12 ml of hydrochloric acid (1+1). Transfer the solution

into a separatory funnel, and proceed the procedures as described above.

3. Results and Discussion

3. 1 Hidride generation and quartz cell atomizer

When the high concentration mode of the instrument was used, reasonable linearity was obtained for the calibration graphs up to 1 µg at the 224.6 nm absorption line, and up to 5 µg at the 254.7 nm line. Because the sensitivity for tin increased with the feed rate of the sample solution, the maximum feed rate(20ml /min) was selected.

The concentration of hydrochloric acid of the hydride generator was tested at 0.3 and 0.6M. Although, the absorbance signal of tin was increased about 20% at 0.3M when compared with 0.6M hydrochloric acid, the acid concentration produced unstable baseline and distorted peaks. Accordingly, 0.6M hydrochloric acid was chosen for this work. The conditioning of argon gas flow rate (0.08 to 0.20 l/min for carrier I, and 0.8–1.2 l/min for carrier II), and temperature (850–1000 °C) of the hydride atomizer were not critical.

The effect of acid concentration on the tin absorbance of a solution containing 0.5 µg/25 ml of Sn was tested by varying the concentration of hydrochloric acid from 0.12 to 3.0M in the sample solution. As shown in Fig. 2, higher absorbance was obtained in lower acidities, and the absorbance decreases markedly against increasing concentration of acid. At lower acidities, the solution of tin was unstable because the element forms easily hydride precipitate by hydrolysis. In this study, oxalic acid was selected to keep suitable acidity for suppression of the hydrolysis, and for elimination of interference from the elements as the following experiments.

The interference of iron (III) on the tin absorbance was observed and elimination by organic acids was examined. Ammonium oxalate or oxalic acid can eliminate the iron (III) interference as shown in Fig. 3, but tartaric acid was not successful. The interferences of copper and nickel on the tin absor-
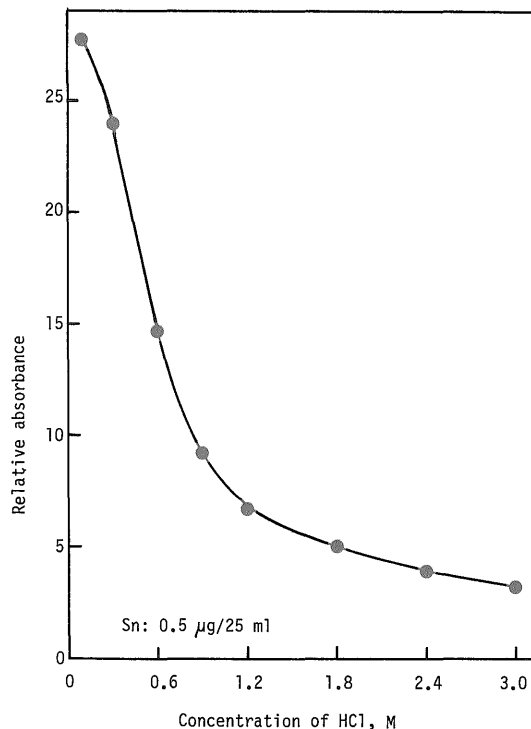

Fig. 2 Effect of hydrochloric acid concentration of the sample solution on tin absorbance.
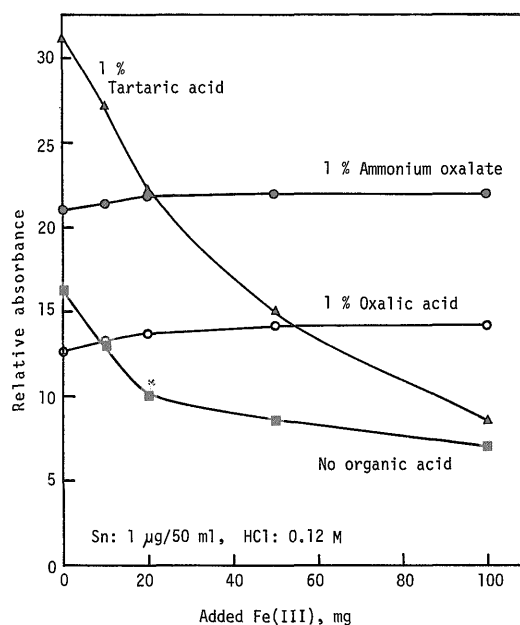

Fig. 3 Interference of iron(III) for tin absorbance and their elimination by tartaric acid, ammonium oxalate and oxalic acid.
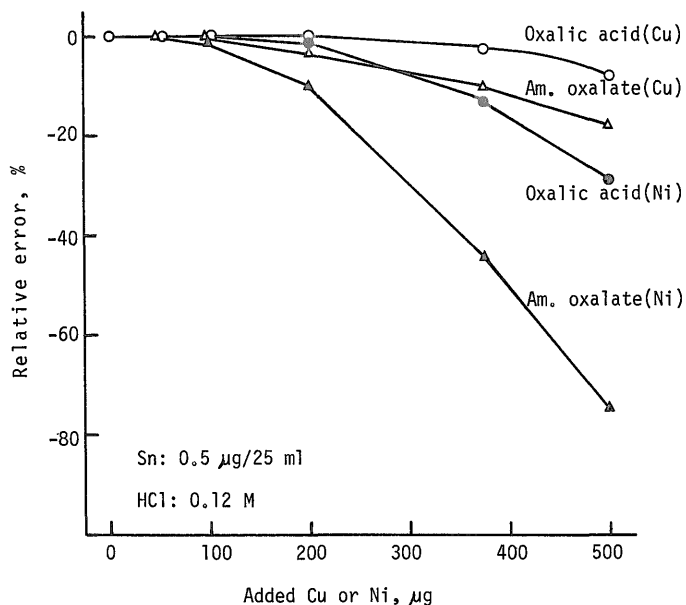
Fig. 4　Interference of copper and nickel for tin absorbance and their elimination by oxalic acid and ammonium oxalate.

bance were also eliminated by the addition of oxalic acid or ammonium oxalate. However, it is likely that oxalic acid was more effective than ammonium oxalate for the suppression of the interferences as given in Fig. 4. Therefore, oxalic acid was used to suppress the interferences and the hydrolysis of tin in the sample solution.

Interferences from other elements were studied at concentrations equal to or greater than those typically found in common silicate rocks and sediments. Although the some enhancing or reducing effects were observed as listed in Table 2, those interferences can be minimized by the addition of aluminium chloride solution, and the restriction of sample taking to less than 0.2 g in the above-mentioned analytical procedures. The reducing interference of fluorine on the tin absorbance were also eliminated by the addition of aluminium chloride solution as shown in Fig. 5.

3. 2　Solvent extraction and carbon tube atomizer

ZHOU *et al.* (1984) has used MIBK(methyl isobutylketone) to extract tin-TOPO complex

Table 2　Effect of various elements on tin absorbance (0.5 μg Sn).

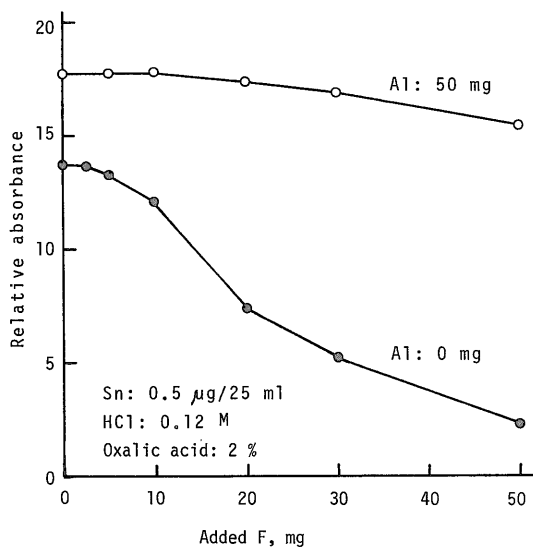| Element	Compound	Amount as element (mg)	Absorbance change (%)
Al	$AlCl_3$	20	+21
		50	+30
		100	+35
Fe	$FeCl_3$	100	+5
Mg	$MgCl_2$	100	+20
Ca	$CaCl_2$	100	−15
Na	NaCl	100	0
K	KCl	100	0
Ti	$TiCl_3$	10	0
Zn	$ZnCl_2$	1	0
Cu	$CuCl_2$	0.5	−10
Co	$CoCl_2$	0.5	−14
Ni	$NiCl_2$	0.5	−6
Pb	$Pb(NO_3)_2$	0.5	−5
V	NH_4VO_3	0.5	−10
Pt	H_2PtCl_6	0.05	−10
Bi	$Bi(NO_3)_3$	0.05	−11
Sb	$SbCl_3$	0.005	0
As	$AsCl_3$	0.002	−8

Fig. 5 Interference of fluorine for tin absorbance and their elimination by aluminium.

from the sample solution. However, it is considered that the method is undesirable because of the large solubility of MIBK in aqueous solution. Accordingly, in this study, butyl acetate which has smaller solubillity than MIBK was selected as an extractant.

In the concentration range of hydrochloric acid from 0.3 to 3.6M, there was no clear difference on the extraction of tin-TOPO complex by butyl acetate, and more than 99% of tin was extracted. Fluorine suppresses the extraction of tin. The interference from fluorine, however, can be avoided by the extraction from the higher concentration of hydrochloric acid and the addition of aluminium.

The extraction of tin-TOPO complex from a solution of 2.4M hydrochloric acid containing 40 mg of aluminium as chloride was not interfered by fluorine up to 200 mg. Molybdenum was extracted together with tin, and more than 0.2 mg of the element suppresses the tin absorbance. However, the amounts of molybdenum in the geological materials studied are well below the interfering level.

The extraction of 2 μg tin was not interfered by the coexistence up to 1000 mg of perchloric acid, nitric acid, sulfuric acid, phosphoric acid, 200 mg of boric acid, 100 mg of sodium, potassium, magnesium, calcium, manganese, iron (II) or aluminium, 20 mg of titanium, and 1 mg of copper, lead, zinc, cobalt, nickel, chromium, vanadium, uranium, zirconium or platinum. If the fusion procedure was adopted for sample dissolution, gelatinous silica often appeared in the organic solvent. However, tin was not contained in the gelatinous silica which can be separated readily from the organic solvent by using a centrifugal machine.

3. 3 Decomposition of sample

As for the determination of tin in common silicate rocks and sediments, the samples can be completely decomposed by digestion with perchloric, nitric, and hydrofluoric acids (TE-RASHIMA, 1975) or sulfuric and hydrofluoric acids (CHAN and BAIG, 1982). Analytical results by the acids digestion and the fusion method for seven geological reference samples are listed in Table 3. The agreement between two methods for the soils, hot spring deposit,

Table 3 Comparison of results for tin(ppm) in selected geological samples by different dissolution methods.

Samples	Acids digestion ($HClO_4 + HNO_3 + HF$)	Fusion ($Na_2CO_3 + H_3BO_3$)	Other values
GXR–2 Soil	2.3, 2.2, 2.0, 2.1	2.2, 2.1	1.98*
GXR–3 Hot spring deposit	0.9, 1.1, 0.9	0.9, 1.0, 0.8, 1.0	0.94*
GXR–5 Soil	2.1, 2.0, 1.8, 1.9	2.0, 2.0	2.84*
1633a Coal fly ash	6.4, 6.2, 6.5	6.0, 6.4	
Nod–A–1 Manganese nodule	3.6, 4.1, 3.2, 3.7	3.8, 3.2, 3.5	
176/2 Manganese ore	2.0, 2.5, 2.2, 2.3	2.2, 2.5	
800–3 Iron ore	54, 59, 56	118, 112, 114	120**

*After ZHOU et al. (1984).
**Certificate value, Iron and Steel Institute of Japan.

coal fly ash, manganese nodule, manganese ore are fairly good. However, the results of the acids digestion for the iron ore (hematite) is clearly lower than those of the fusion method. This suggests that some geological samples may not be completely decomposed by the acid digestion. The analytical results of tin in other geological reference samples by the different dissolution methods have been reported (Terashima, 1982). The results indicate that the majority of common geological samples as rocks, sediments and minerals can be decomposed by the digestion of acid mixture including hydrofluoric acid, and the fusion method with sodium carbonate and boric acid was required for only several samples containing refractory tin-bearing minerals as greisen, spodumene, sillimanite schist and jasperoid (Terashima, 1982).

When the sample to be analysed has high content of non-carbonate carbon, an ashing procedure was required to remove the carbon before the fusion procedure. If the ashing procedure was omitted, the values of tin were reduced to about half in most cases. This may arise from the formation of an alloy of tin and platinum during the fusion procedure. There was no ashing procedure in the sample dissolution with acids, so that the noncarbonate carbon was not completely removed from samples such as shale and coal fly ash, but the residue did not have any effect on the hydride generation or solvent extraction procedures.

3. 4 Analysis of geological reference samples

Results obtained for tin in eighteen geological reference samples by acid digestion-hydride generation and quartz cell atomizer are given in Table 4, and compared with reported values. The reported values were obtained by atomic absorption spectrometry with a solvent extraction and graphite furnace atomizer (Zhou et al., 1984), or argon-hydrogen flame (Terashima, 1982), or hydride generation and

Table 4 Analytical results for tin(ppm) in eighteen geological reference samples by hydride generation and quartz cell atomizer.

Samples		This study*	Zhou et al. (1984)	Terashima (1982)	Chan et al. (1982)	
					Digestion	Fusion
USGS	BHVO–1 Basalt	1.92±0.16	1.74	1.90	1.9	1.8
	MAG–1 Marine mud	3.31±0.20	1.90	2.98	3.7	3.2
	QLO–1 Quartz latite	2.32±0.15	2.34	2.14	2.3	2.4
	RGM–1 Rhyolite	4.20±0.22	3.65	3.78	4.4	4.4
	SCo–1 Cody shale	3.41±0.18	3.22	3.02	3.7	3.9
	SDC–1 Mica schist	3.13±0.20	2.83	2.68	3.0	3.2
	STM–1 Syenite	7.54±0.36	9.02	6.70	7.2	6.7
NBS	69A Bauxite	8.51±0.40	—	—	—	—
	97a Clay, flint	6.90±0.28	—	6.16	—	—
	98a Clay, plastic	5.76±0.30	—	5.25	—	—
GSJ	JA–1 Andesite	0.78±0.10	—	0.8**	—	—
	JB–1a Basalt	2.01±0.12	—	—	—	—
	JB–2 Basalt	0.56±0.08	—	0.5**	—	—
	JB–3 Basalt	0.86±0.10	—	0.8**	—	—
	JG–1a Granodiorite	4.21±0.23	—	—	—	—
	JGb–1 Gabbro	0.36±0.06	—	0.4**	—	—
	JR–1 Rhyolite	2.70±0.15	—	2.6**	—	—
	JR–2 Rhyolite	3.18±0.18	—	2.9**	—	—

*Average value of 3–5 determinations with standard deviation.
**After Terashima et al. (1984).

quartz cell atomizer after acids digestion or lithium metaborate fusion (CHAN and BAIG, 1982). The agreement between the present results and the reported values are fairly good. The results of this work for fourteen geological reference samples by solvent extraction and carbon tube atomizer or nitrous oxide-acetylene flame are listed in Table 5 for comparison with the values of ZHOU *et al.* (1984); agreement is generally good.

The relative standard deviatrion are calculated to be 14% or less for the determination of more than 0.5 ppm of tin by the present hydride genelation or solvent extraction separation with atomic absorption spectrometry. The limit of detection in the determination of tin is 0.1 ppm by hydride generation and quartz

Table 5 Analytical results for tin(ppm) in fourteen geological reference samples by solvent extraction and carbon tube atomizer.

Samples		This study*	ZHOU *et al.* (1984)
GSJ	JP–1 Peridotite	0.05±0.01	—
USGS	GXR–1 Jasperoid	59.0±1.6**	52.4
	GXR–2 Soil	2.15±0.13	1.98
	GXR–3 Hot spring deposit	0.97±0.12	0.94
	GXR–4 Porphyry copper ore	6.10±0.14	4.79
	GXR–5 Soil	1.95±0.13	2.84
	GXR–6 Soil	1.55±0.13	0.86
	Nod–A–1 Manganese nodule	3.65±0.37	—
	Nod–P–1 Manganese nodule	3.43±0.39	—
NBS	la Limestone	2.58±0.10	—
	120b Phosphate rock	0.41±0.05	—
	1633a Coal fly ash	6.36±0.15	—
BCS	176/2 Manganese ore	2.25±0.20	—
JSS	800–3 Iron ore	115±3**	120***

*Average value of 3–5 determinations with standard deviation.
**Determined by nitrous oxide-acetylene flame after fusion.
***See notes in Table 3.

cell atomizer, and 0.04 ppm by solvent extraction and carbon tube atomizer for 0.5 g of a given sample. The time required for the determination of tin in ten samples estimates 4 hours or less.

3. 5 Conclusions

For the determination of tin by present atomic absorption spectrometry, the solvent extraction and carbon tube atomizer is more sensitive than the hydride generation and quartz cell atomizer. However, the analytical procedures of the solvent extraction and carbon tube atomizer are rather complicated than those of the hydride generation and quartz cell atomizer. Therefore, the application of the carbon tube atomizer will be restricted to samples having very low tin content and those containing a large amount of interfering elements. In order to dissoluve samples, the acids digestion method is more convenient than the fusion method for routin work, moreover the method gives higher sensitivity due to the use of large amount of samples. For the sample which is known to contain refractory tinbearing minerals, fusion procedure is recommended. The methods studied in this work can be applied to tin analysis for a great variety of geological materials such as rock, soil, clay, bauxite, limestone, phosphate, coal fly ash, manganese nodule and iron ore.

References

CHAN, C. Y. and BAIG, M. W. A. (1982) Semi-automatic method for determination of total tin in rocks. *Anal. Chim. Acta*, vol. 136, p. 413–419.

IKEDA, M., NISHIBE, J. and NAKAHARA, T. (1981a) Investigation of some fundamental conditions for the determination of arsenic, lead and tellurium with continuous hydride generation-atomic absorption spectrometry. *Bunseki Kagaku*, vol. 30, p. 368–374.

———, ———, ——— (1981b) Investigation of some fundamental conditions for the determination of antimony, tin, selenium and bismuth by continuous hydride generation-flame less atomic absorption spectrometry. *Bunseki Kagaku*, vol. 30, p. 545–547.

SUBRAMANIAN, K. S. and SASTRI, V. S. (1980) A rapid

hydride-evolution electrothermal atomic-absorption method for the determination of tin in geological materials. *Talanta*, vol. 27, p. 469–472.

TERASHIMA, S. (1975) Determination of micro-amounts of tin in silicates by atomic absorption spectrometry with an argon-hydrogen flame. *Bunseki Kagaku*, vol. 24, p. 319–321.

———— (1982) Determination of trace amounts of tin in seventy-three geochemical reference samples by atomic absorption spectrometry. *Geostandards Newsletter*, vol. 6, p. 77–81.

————, YAMASHIGE, T. and ANDO, A. (1984) Determination of major and minor elements on the six GSJ rock reference samples. *Bull. Geol. Surv. Japan*, vol. 35, p. 171–177.

ZHOU, L., CHAO, T. T. and MEIRE, A. L. (1984) Determination of total tin in geological materials by electrothermal atomic absorption spectrophotometry using a tungsten-impregnated graphite furnace. *Talanta*, vol. 31, p. 73–76.

原子吸光法による地質試料中微量スズの定量

寺島　滋

要　旨

原子吸光法による地質試料中の微量スズの迅速かつ高精度な定量法を確立した．一般の岩石，堆積物試料は過塩素酸，硝酸，フッ化水素酸で分解し，希塩酸及びシュウ酸溶液で溶解する．一定量の塩化アルミニウムを加えて試料溶液とし，水素化ホウ素ナトリウム溶液及び希塩酸と共に水素化物発生装置に導入してスズの水素化物を発生させる．石英管アトマイザーを用いて原子化し，スズを定量する．

銅，コバルト，ニッケル等を多量に含む鉱石類や難溶性鉱物が含有される試料中のスズは，溶媒抽出分離—炭素管アトマイザー法で定量する．試料を酸分解法又は炭酸ナトリウムとホウ酸による融解法で処理した後希塩酸に溶解する．一定量の塩化アルミニウム溶液を加えた後，トリオクチルホスフィン(TOPO)—酢酸ブチル溶液で抽出し，有機相中のスズを炭素管アトマイザーを用いて定量する．

水素化物発生—石英管アトマイザー法を用いた場合は0.1 ppm，溶媒抽出—炭素管アトマイザー法では0.04 ppmまで定量可能であり，10試料についての分析所要時間は前者の場合約3時間，後者では約4時間であった．また，0.5 ppm以上のスズの定量における変動係数はいずれの方法でも14%以下であった．各種けい酸塩岩石，堆積物，ボーキサイト，石灰石，リン鉱石，コールフライアッシュ，マンガンノジュール，マンガン鉱石，鉄鉱石等の地質標準試料の分析を行って良好な結果を得た．