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ANTIMONY IN MUNICIPAL WASTE

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Abstract

Antimony content in municipal waste was studied. Sampled municipal waste was dried, crushed and analyzed. Antimony determinations were performed by Kjeldahl decomposition − batch-hydride generation spectrometry and neutron activation analysis. Overall content of antimony in waste was 40−50 g/t raw waste. It was estimated that 20 % of the annual production of antimony was discarded as municipal waste in Japan. Leaching of antimony from antimony−added materials may occur, because "small tips" involved considerable amounts of antimony.

INTRODUCTION

Interest in antimony has been increasing because of its potential chronic toxicity[1]. Japan government has issued the guideline of 2 μg Sb/L in natural water and drinking water in 1993. Antimony pollution on Japanese rivers was already revealed by our monitoring study in

Yodo basin, which exceeded sometimes the guideline concentration[2].

The annual antimony production is ca.10,000 tons in Japan mostly for use as fire–retardant[3]. Since there is no reuse or recycling, it is finally discarded. Three reports have so far appeared in connection with antimony in waste[4–6]. Those workers presented antimony concentration of 8–40 gSb/t. Artificial textiles[6] as well as "fines"[5] were suggested to be a considerable source of antimony.

Municipal waste analysis by local governments in Japan can offer valuable information. We utilized samples from Osaka city[7] to investigate how much antimony is involved and which component mainly contribute.

For determination of antimony in municipal waste samples, Kjeldahl decomposition – batch hydride generation atomic absorption spectrometry(HGAAS) and neutron activation analysis(NAA) were applied. NAA is an ideal method because it is free from digestion process, however, the allowed sample number is limited since it needs an atomic reactor. Hence, HGAAS should be a widely usable method, with NAA as a cross–check tool. We report here the analytical data, discuss the overall amount, main source and leaching of antimony.

EXPERIMENTAL

Sample

Analytical samples were taken from 10 municipal waste incinerators in Osaka city during January to March in 1996. The procedure of the sample collection and preparation were described elsewhere[7]. Briefly, collected samples were dried at 85 ℃ for three days, followed by sorting and crushing. Ten sorting categories(six combustibles and four incombustibles) were used.

Each combustible component was individually analyzed by HGAAS(compositional study). In parallel, "mixed combustibles" were prepared according to the original proportion for overall analysis, which were also analyzed by both HGAAS and NAA(overall study).

Analytical methods

The procedure of Kjeldahl decomposition – HGAAS was described in detail elsewhere[8]. Briefly, 0.5−1 g of sample was added with 30 mL of sulfuric acid and 2 g of catalyst (mixture of copper sulfate and potassium sulfate(2:5)), and heated in a Kjeldahl flask on a burner. After the sample was brought to 100 mL, a portion of 0.05−1.0 mL was analyzed by HGAAS.

NAA was carried out in Kyoto university research reactor, Kumatori, Osaka, Japan [8]. As a calibration sample, BCR−176(city waste incineration ash, the concentration of antimony was 412 mg/kg)[10] was used. Gamma−ray of 1691 keV at 1 month after the irradiation was used to quantify.

RESULTS AND DISCUSSION

Evaluation of analytical method

All analytical results are shown in Table 1(compositional study wth HGAAS) and Table 2(overall measurement with HGAAS and NAA), in which the amount of each composition in the waste and the amount of antimony loaded by each composition are listed, too. Antimony content in municipal waste are presented in Fig. 1 comparing the results obtained by three methods. Though the variation of the data between different methods is not trivial, it could be concluded Kjeldahl method brought sufficient decomposition and no loss to antimony analysis. It was difficult to combine various materials(different in water affinity and in density) homogeneously.

Table 1 Antimony in each composition in municipal waste

Method	Sample		Plant number No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8	No.9	No.10	Average ±	std(n-1)
HGAAS														
	Kitchen Garbage													
	Amount of component	(kg/t raw waste)	42.3	54.6	23.8	20.0	49.9	56.9	55.0	64.2	87.5	18.7	47.3 ±	19.7
	Concentration of Sb	*(mg/kg)*	*2.7*	*3.5*	*1.7*	*1.3*	*0.8*	*1.2*	*0.2*	*26.2*	*0.6*	*0.4*	*3.9* ±	*7.2*
	Amount of Sb	(g/t raw waste)	0.1	0.2	0.0	0.0	0.0	0.1	0.0	1.7	0.0	0.0	0.2 ±	0.5
	Paper													
	Amount of component	(kg/t raw waste)	332.1	157.0	337.5	393.7	139.8	155.5	121.0	324.9	152.3	230.7	234.5 ±	92.7
	Concentration of Sb	*(mg/kg)*	*7.8*	*9.3*	*8.3*	*2.8*	*10.0*	*10.1*	*8.7*	*no data*	*1.6*	*4.9*	*7.0* ±	*3.0*
	Amount of Sb	(g/t raw waste)	2.6	1.5	2.8	1.1	1.4	1.6	1.0	0.0	0.2	1.1	*1.5* ±	*0.7*
	Textile													
	Amount of component	(kg/t raw waste)	27.2	30.5	53.5	16.4	3.5	3.8	45.5	73.1	8.2	32.4	29.4 ±	20.7
	Concentration of Sb	*(mg/kg)*	*14.3*	*23.5*	*53.3*	*54.3*	*8.2*	*15.1*	*44.6*	*3717.6*	*6.1*	*19.2*	*395.6* ±	*1055.9*
	Amount of Sb	(g/t raw waste)	0.4	0.7	2.8	0.9	0.0	0.1	2.0	271.8	0.0	0.6	27.9 ±	77.5
	Wood and Leaves													
	Amount of component	(kg/t raw waste)	30.0	19.7	26.2	15.7	153.5	42.9	72.5	17.0	15.5	61.5	45.4 ±	38.8
	Concentration of Sb	*(mg/kg)*	*1.3*	*5.7*	*2.1*	*1.6*	*1.9*	*1.0*	*1.2*	*6.3*	*2.6*	*0.8*	*2.5* ±	*1.8*
	Amount of Sb	(g/t raw waste)	0.0	0.1	0.1	0.0	0.3	0.0	0.1	0.1	0.0	0.0	0.1 ±	0.1
	Plastic, Rubber and Leather													
	Amount of component	(kg/t raw waste)	68.0	88.3	124.3	66.6	87.7	74.9	93.5	129.0	81.0	147.5	96.1 ±	25.2
	Concentration of Sb	*(mg/kg)*	*23.7*	*149.8*	*17.9*	*11.9*	*59.7*	*17.9*	*501.9*	*44.7*	*56.3*	*208.5*	*109.2* ±	*137.7*
	Amount of Sb	(g/t raw waste)	1.6	13.2	2.2	0.8	5.2	1.3	46.9	5.8	4.6	30.8	11.2 ±	14.0
	Small Tips (to pass 5mm screen)													
	Amount of component	(kg/t raw waste)	44.2	146.7	100.3	70.1	122.9	129.2	124.5	52.0	58.7	73.9	92.2 ±	33.4
	Concentration of Sb	*(mg/kg)*	*62.9*	*479.6*	*64.9*	*22.7*	*60.6*	*19.1*	*7.2*	*120.2*	*12.5*	*36.0*	*88.6* ±	*128.0*
	Amount of Sb	(g/t raw waste)	2.8	70.4	6.5	1.6	7.4	2.5	0.9	6.3	0.7	2.7	10.2 ±	19.3
	Sum of Sb	(g/t raw waste)	7.5	86.1	14.5	4.4	14.5	5.5	51.0	285.6	5.7	35.2	51.0 ±	78.3

Table 2 Overall antimony content in municipal waste

Method Sample		Plant number No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8	No.9	No.10	Average ±	std(n-1)
HGAAS													
Combined Combustible Components													
Amount	(kg/t raw waste)	543.8	496.7	665.6	582.5	557.3	463.2	512.0	660.3	403.2	564.7	544.9 ±	73.9
Concentration of Sb	*(mg/kg)*	*12.9*	*135.5*	*16.7*	*10.7*	*12.5*	*10.3*	*110.0*	*430.1*	*53.9*	*106.2*	*89.9* ±	*116.7*
Amount of Sb	(g/t raw waste)	7.0	67.3	11.1	6.3	6.9	4.8	56.3	284.0	21.7	59.9	52.6 ±	76.9
NAA													
Combined Combustible Components													
Amount	(kg/t raw waste)	543.8	496.7	665.6	582.5	557.3	463.2	512.0	660.3	403.2	564.7	544.9 ±	73.9
Concentration of Sb	*(mg/kg)*	*11.6*	*77.2*	*14.4*	*4.6*	*11.4*	*11.3*	*113.4*	*408.9*	*12.8*	*34.7*	*70.0* ±	*112.4*
Amount of Sb	(g/t raw waste)	6.3	38.3	9.6	2.7	6.4	5.2	58.1	270.0	5.2	19.6	42.1 ±	74.2

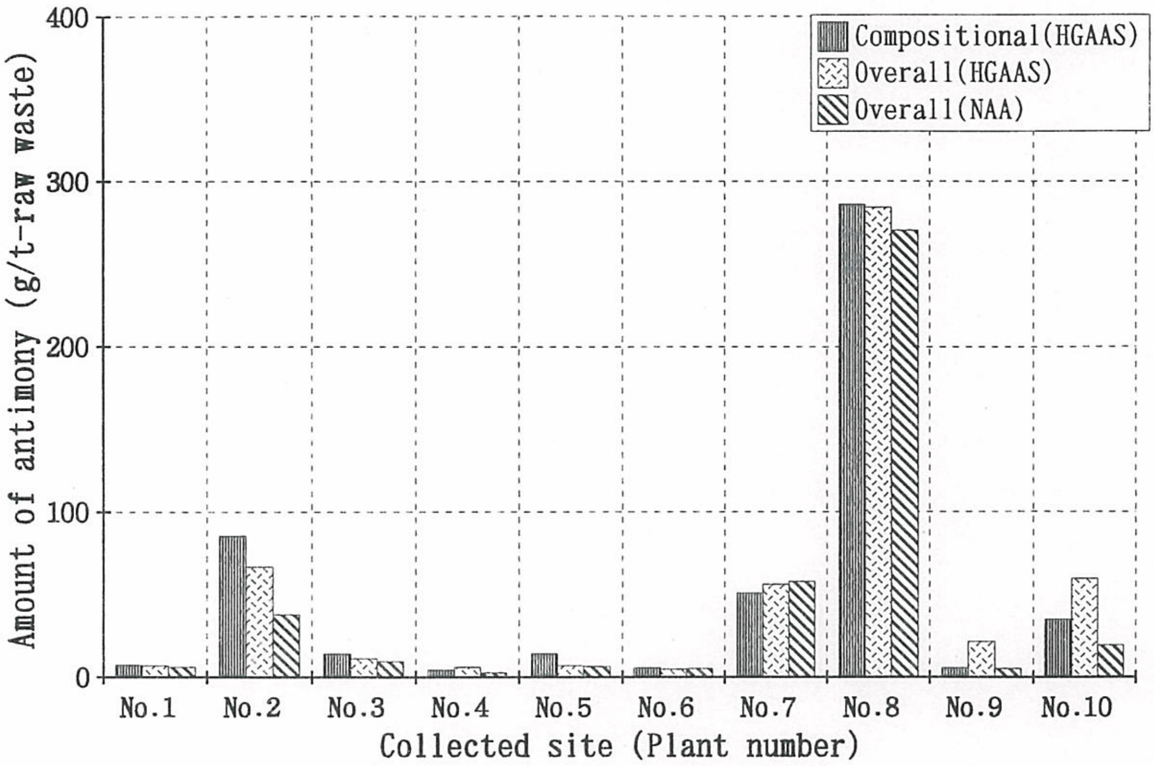

Fig. 1 Antimony content in municipal waste

Amount of antimony in municipal waste

Averaging the overall antimony amount in municipal waste, 40 – 50 gSb/ton raw waste was obtained. This agreed well with our investigation on the mass balance estimation in incinerators[9], in which the estimated antimony amount was 30 – 44 gSb/t. The present value seemed a little higher, however, it can be acceptable variation, considering the highest value(280 gSb/t from No.8) an extraordinary value. Similarly, it also agreed with the surveys conducted in the United States (40 gSb/t−dry)[4] and in Canada (33 gSb/t in average) [5]. The value 7.6 gSb/t reported by Nakamura et al. was considerably lower than ours, though their data was obtained in Japan, too. It may be due to their oxidative digestion procedure with hydrofluoric acid, which might cause some recovery loss of antimony[11–13].

It is interesting to compare this data to the annual production of antimony. Annual municipal waste generation in Japan is 5×10^{7} t/y[13]. Assuming antimony concentration in municipal waste is 40 gSb/t, it can be estimated that 2000 tSb/y is currently disposed as municipal waste. This is 20 % of the annual production of antimony. It must be noted here, industrial wastes, for example, construction debris or shredder dusts from discarded cars or electric apparatuses are not included into the above municipal waste. Those products may contain more antimony as fire–retardants.

Major source of antimony in municipal waste

The antimony concentration level in individual components are presented in Fig.2. Ubiquitous occurrence of antimony was clearly found from the compositional study. Most of "kitchen garbage", "paper" and "wood and leaves" contained antimony less than 10mg/kg. On the other hand, half samples of "textile", "plastic, rubber and leather" and "small tips" showed rather high concentration, namely, larger than 50mg/kg. Moreover, their concentration levels were in a very wide range. The highest concentration of antimony was 3712 mgSb/kg, which was found in "textile" from the plant No.8, while the lowest concentration in textile was 6.1 mg/kg. This difference must due to fire–retardant treatment on synthetic textiles, which was already pointed out by Nakamura et al[6]. At the same time, it is natural that cotton or silk does not contain much antimony.

Antimony was also found in plastics in considerably concentrations. The constant occurrence of antimony in "plastic, rubber and leather" could suggest wide–ranging use. Although most of antimony production in Japan is in the form of Sb_2O_3 as a fire–retardant, its application might not be limited to fire–retardant additives. Usage as a pigment or transparency–promoter should be suspected.

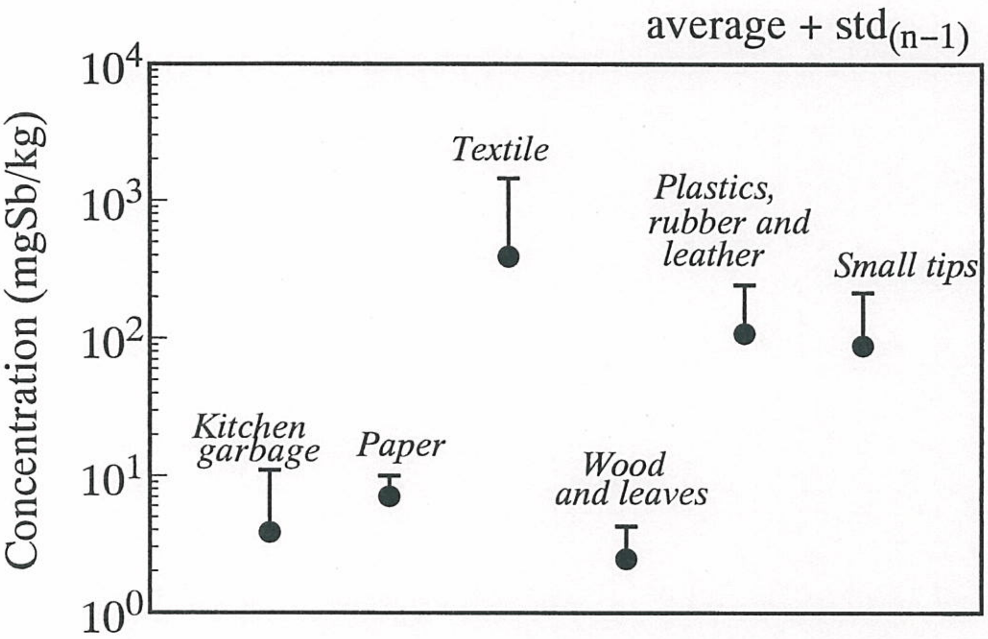

Fig. 2 Antimony concentration level in individual components

Leaching of antimony

"Small tips" showed constantly rather high concentration, which agreed to the report of Rigo et al[5], who claimed "fines" contributed considerably. Both "small tips" and "fines" mainly consist of sand and small food residue, which do not carry much antimony in nature. We suppose leaching of antimony from antimony−added synthetic products may occur, afterwards, they might be adsorbed by "small tips".

CONCLUSIONS

Antimony in municipal waste sample was investigated using three analytical procedures. The analytical results suggested Kjeldahl decomposition applicable to antimony analysis. Overall amount of antimony was 30−50 gSb/t−raw waste.

Assuming this value to be an average in Japan, it was calculated ca. 20 % of the national annual production was discarded as municipal waste. In other words, 80 % of annually produced antimony may be disposed in other ways, e.g. as industrial waste.

Synthetic textile, plastics were found to be the main source of antimony as fire−retardant and pigment. Furthermore, the comparatively constant occurrence in "small tips" could not be explained by antimony usage, but might be owing to leaching from antimony−added products in raw waste.

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