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Analytical methods for airborne arsine, silane and dichlorosilane by adsorption sampling and AA spectrophotometry

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Analytical methods for arsine, silane and dichlorosilane by adsorption sampling and elemental analysis with graphite furnace AA were studied to establish convenient methods for atmospheric contamination surveys. This study included the following five items: (1) primary selection of adsorbents applicable to adsorption sampling; (2) examination of the adsorption capacities of the adsorbents for the gases; (3) improvement of the adsorbents by chemical modification; (4) desorption of the gases adsorbed on the adsorbents with solvents; and (5) quantitative analysis of arsenic and silicon in the solutions.

Experimental results showed that active carbon made from synthetic thermosetting resin beads contained no arsenic and little silicon as impurities. This active carbon by itself was proved to adsorb arsine and dichlorosilane, but not silane. Impregnation with sodium hydroxide of the active carbon improved the adsorption capacity for all three gases. Refined silica gel, free from arsenic contamination, did not adsorb arsine by itself but potassium permanganate impregnation produced an adsorption capacity for arsine.

The adsorbed arsine on the active carbon was desorbed into a hot dilute nitric acid solution with high efficiency (over 90%), but arsine adsorbed on sodium hydroxide impregnated active carbon or on potassium permanganate impregnated silica gel was dissolved into various solutions only at lower efficiencies. Silane adsorbed on sodium hydroxide-impregnated active carbon was desorbed with hot water with an efficiency higher than 90%. Dichlorosilane adsorbed on the active carbon with or without sodium hydroxide impregnation was desorbed with a nitric acid solution with efficiency of 85%. The lower determination limit for arsine able to discriminate from background interference of arsenic was 0.005 ppm, and those for silane and dichlorosilane were each 0.05 ppm for 3-dm^3 air samples.

Keywords: Analysis, arsine, silane, dichlorosilane, adsorption, sampling, environment, monitoring

1 INTRODUCTION

Industrial technologies for manufacturing semiconductor materials and fine ceramics consume various kinds of hydrides, halides and organocompounds of tri-, tetra- and quinqua-valent elements. Silane is used in the greatest amounts and arsine is one of the most toxic gases among them.

Most of these gases are not very stable in contact with atmospheric oxygen or moisture but their contamination in air should be measured because of their high toxicities. Arsine and silane are known to be acutely toxic and the permissible exposure limit concentrations (PELs) are recommended as 0.05 ppm for arsine and 5 ppm for silane by the American Conference of Governmental Industrial Hygienists (ACGIH) as Threshold Limit Values (TLV-TWA). The Japan Association of Industrial Health also recommends the same value for arsine. Both authorities do not show a PEL value for dichlorosilane.

The present work is an experimental study on the quantitative analytical methods for airborne arsine, silane and dichlorosilane, which are useful for surveys of atmospheric contamination in and around industrial workplaces where these gases are used. The National Institute of Occupational Safety and Health (NIOSH) of the United States has published an adsorption sampling method for arsine using coconut-shell active carbon.[1] Costello *et al.* also reported sampling method for arsine coexistent with arsenic oxide particles using coconut-shell active carbon with a sodium

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carbonate-impregnated filter.[2] But coconut-shell active carbon is contaminated with arsenic, which interferes with the analysis of adsorbed arsine, as shown in our previous report[3] and also in this study. No adsorption sampling methods for silane and dichlorosilane have been published before our study.[4] Wet sampling methods have also been applied to collect these gases for field surveys,[5] but sampling efficiencies vary with the air drawing conditions and the sampling apparatus is not amenable for field surveys. We intended to establish or to improve adsorption sampling methods and analytical methods for these gases which are sensitive at concentration ranges lower than the PELs of these gases.

2 EXPERIMENTAL

The adsorbents submitted for the primary selection in this study were those presented in Table 1, i.e. three kinds of synthetic thermosetting resin active carbon with different lot numbers (Sumitomo Bakelite Co. Ltd, Tokyo), five kinds of coconut-shell active carbon (PCBs from Calgon Co., Pittsburgh; HGH from Takeda Chemical Co. Ltd, Osaka; and Ys from Hokuetsu Tanso Co., Yokohama), five kinds of silica gel (A, Bs and ID from Fuji-Davison Chemical Ltd, Kasugai; EB from Colcoat Co. Ltd, Tokyo), three kinds of polymer bead (XADs from Supelco Inc., Bellefonte; TENAX from ENKA Research Institute) and a membrane filter TM-80 (plain and white, 0.8-μm pore size and 25-mm diameter from Toyo Roshi Co. Ltd, Tokyo). Their specific surface areas were determined by the BET method applied to the adsorption isotherms of nitrogen at −196°C. The levels of extractable arsenic and silicon were determined by graphite furnace AA analysis of the extracts. For this purpose, a specimen (200 mg) of each adsorbent was immersed in $4\,cm^3$ of the dissolving solution and treated at around 80°C with/without ultrasonic vibration for a time up to 2 h. The membrane filter was also examined for its impurity content, because it is used to collect airborne particles coexistent with the gases.

To improve the adsorbents, various kinds of chemicals were impregnated. Those chemicals used for impregnation were chosen amongst reagents utilized for chemical colorimetry of the gases and the gas traps with reference to their reactivities towards the gases. The impregnation was performed as follows. The calculated amount of a chemical was dissolved in sufficient water to immerse the adsorbent, which was poured into the solution; then the mixture was evacuated with mild heating to 110°C with a cold trap.

Table 1 Basic properties of adsorbents

Adsorbent	Specific surface area ($m^2\,g^{-1}$)	Impurity content[a] Arsenic ($\mu g\,g^{-1}$)	Silicon ($\mu g\,g^{-1}$)
Active carbon from coconut-shell			
Y-10	946	0.032	425
Y-25	1309	0.104	953
PCB 12 × 30	1090	0.037	340
PCB 20 × 40	812	0.066	178
HGH 660	1573	0.085	408
Active carbon from synthetic resin			
M934	1522	0.0013	10.28
M915	1347	0.0010	3.38
M145	871	ND	0.84
Silica gel			
A-type	511	ND	—
B-type, AW	482	ND	—
B-type, NAW	450	ND	—
ID-type, NAW	296	ND	—
EB-type	654	ND	—
Polymer beads			
XAD-4	792	ND	7.20
XAD-7	320	ND	48.5
TENAX GC	573	—	9.84
Others			
Membrane filter (TM-80)		0.0002 /sheet	0.788 /sheet

Abbreviation: ND, net detected

[a] The values are the averages of six measurements for each adsorbent.

The adsorption capacity of each adsorbent for arsine, silane or dichlorosilane was measured by means of a train of equipment, as shown in Fig. 1. The standard gases (100 ppm diluted with nitrogen) were purchased as cylinders, and they were further diluted with nitrogen or purified air to produce the test gases and were kept in plastic bags for short-term storage. The test gas in a bag was drawn by a pump through an adsorbent bed, an electrochemical gas sensor and a flowmeter connected in series at a given flow rate. The sensor was a Type GDS-DB-1 (Gastec Corp., Ayase), which detected breakthrough of the test gas at the exit of the tube.

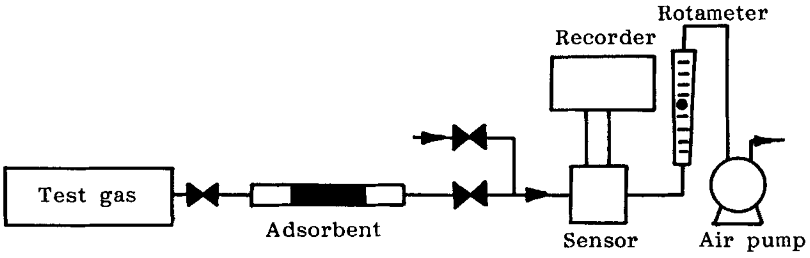

Figure 1 Apparatus for adsorption capacity measurements.

Desorption of arsenic or silicon from the adsorbents which had previously adsorbed arsine, silane or dichlorosilane was carried out by immersing the adsorbents into various solutions with heat and/or ultrasonic treatment, followed by measurements of arsenic and silicon concentrations in the supernatants.

Quantitative analysis of arsenic and silicon was performed with flameless AA using a Perkin–Elmer Model Zeeman/5000 System atomic absorption spectrophotometer with a pyro-coated graphite tube with an autosampler and its sequencer (AS-40) and a furnace temperature programmer (HGA-500). The graphite furnace temperature programs adopted for arsenic and silicon are shown in Table 2. Quantitative determination of arsenic could be carried out in the range down to 1 ng cm^{-3} in 0.01 mol dm^{-3} nitric acid solution with nickel ions (20 μg cm^{-3}) as a modifier with a coefficient of variation (CV) of 28% ($n=6$) at 1 ng cm^{-3} and with a CV of 3% above 10 ng cm^{-3}. However, in the presence of reducing agents such as hydroxylamine or ammonium ions or in the presence of chloride ions, the amount of arsenic detected decreased to lower concentrations than that calculated. The optimum atomization temperature varied depending on the concentration of the added nickel ions. Silicon is an element with a high boiling point and also it forms a less volatile carbide which decomposes at about 2700°C. To cope with this property, a maximum atomization temperature of 2800°C was adopted. The absorbance profiles of silicon during the atomization step at various atomization temperatures are shown in Fig. 2. Another problem in the AA of silicon in the presence of a large amount of sodium carbonate is the possible explosion of carbonate ions, which was removed by adopting temperature programme with two charring steps, i.e. char 1 at 900°C and char 2 at 1400°C. The determination of 50 ng Si cm^{-3} was performed at a CV of 1.4% ($n=6$). However,

Table 2 Operating conditions of the graphite furnace AA

Arsenic

	Dry	Char	Atomize	Clean
Temperature, °C	120	300	2300	2400
Ramp time, s	10	10	1	1
Hold time, s	20	20	4	3
Internal gas flow, $cm^3\,min^{-1}$	300	300	50	300

Silicon

	Dry	Char	Char 2	Atomize	Clean
Temperature, °C	120	900	1400	2800	2800
Ramp time, s	10	10	10	1	1
Hold time, s	20	30	20	2	1
Internal gas flow, $cm^3\,min^{-1}$	300	300	300	50	300

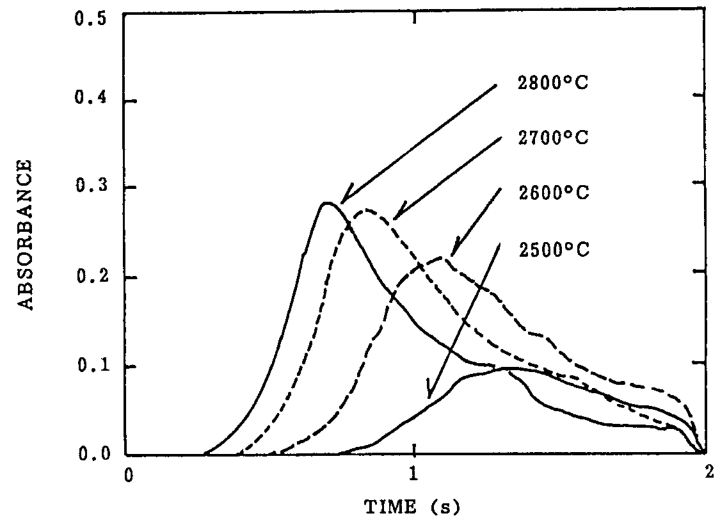

Figure 2 Absorbance of silicon observed by graphite furnace AA at various atomization temperatures.

graphite furnace AA for silicon was accompanied by a slight deflection of the calibration curve at a silicon concentration range lower than 1 μg cm^{-3}.

3 RESULTS

3.1 Primary selection of adsorbents

The adsorbents examined showed various surface areas, as shown in Table 1. It is noted that the active carbons from synthetic resin had similar surface areas to that from coconut shell. Among the silica gels, EB was the product with the largest surface area.

To determine the contaminations of the adsorbents, arsenic in the adsorbents was dissolved in a hot nitric acid solution (0.01 mol dm^{-3}) with ultrasonic vibration, and silicon was dissolved in a hot sodium hydroxide solution (0.2 mol dm^{-3}). Arsenic and silicon concentrations in the extracts increased with time, but they almost attained constant concentrations after 60 min, except for highly contaminated specimens. The amounts of arsenic and silicon in the supernatants after incubation for 60 min were determined and are presented in Table 1. These results show that the active carbon from synthetic resins is not contaminated with arsenic and only slightly with silicon. Most of the silica gels are also free from arsenic contamination.

3.2 Adsorption capacities of the adsorbents for the test gases

Each of two kinds of synthetic-resin active carbon (M934 and M915, 150 mg) and a silica gel (EB, 150 mg) were packed in a glass tube with 4 mm inside diameter, sealed with porous polyethylene plugs at both sides, and submitted to adsorption examination against an arsine test gas flow. The test gas was 0.5 ppm in concentration and drawn at the rate of 500 cm^3 min^{-1}. The escaping arsine concentration at the exit of the tube was recorded along with the time, as shown in Fig. 3. The active carbon showed adsorption capacities for arsine but silica gel EB did not.

Similar adsorption examinations were performed on active carbon for silane and dichlorosilane. The active carbon adsorbed dichlorosilane but not significant amounts of silane, as shown in Figs 4–6.

Polymer beads did not show significant adsorption capacities for these gases. These adsorbents were not submitted to further examination for chemical modifications, because these materials were not inert to the chemicals.

3.3 Improvement of the adsorbents by chemical modifications

Arsine

Impregnation of sodium hydroxide (10 wt %) on a synthetic resin active carbon, M915, promoted the adorption capacity for arsine. As shown in Fig. 3, this adsorbent did not show an adsorption

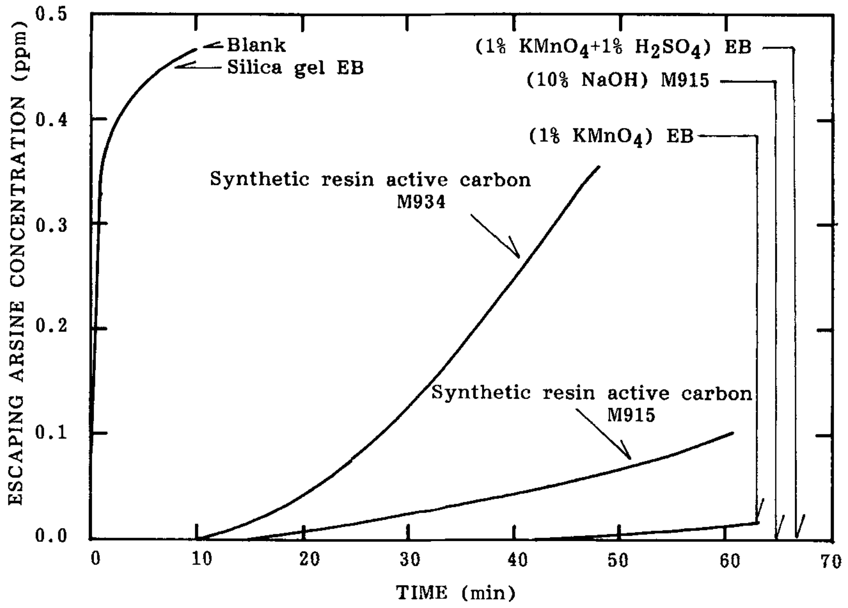

Figure 3 Breakthrough curves of arsine test gas from adsorbent beds. Arsine: 0.5 ppm, 500 $cm^3 min^{-1}$; adsorbent: 150 mg.

breakthrough for arsine test gas at 0.5 ppm until after 60 min from the start of test gas drawing. Silica gel EB with potassium permanganate with or without sulphuric acid also showed an adsorption breakthrough time longer than 40 min for the same arsine test gas.

Silane

Sodium hydroxide impregnation of the synthetic-resin active carbon produced a certain adsorption capacity for silane, and the adsorption breakthrough time was extended with increasing amounts of sodium hydroxide loaded as shown in Fig. 4.

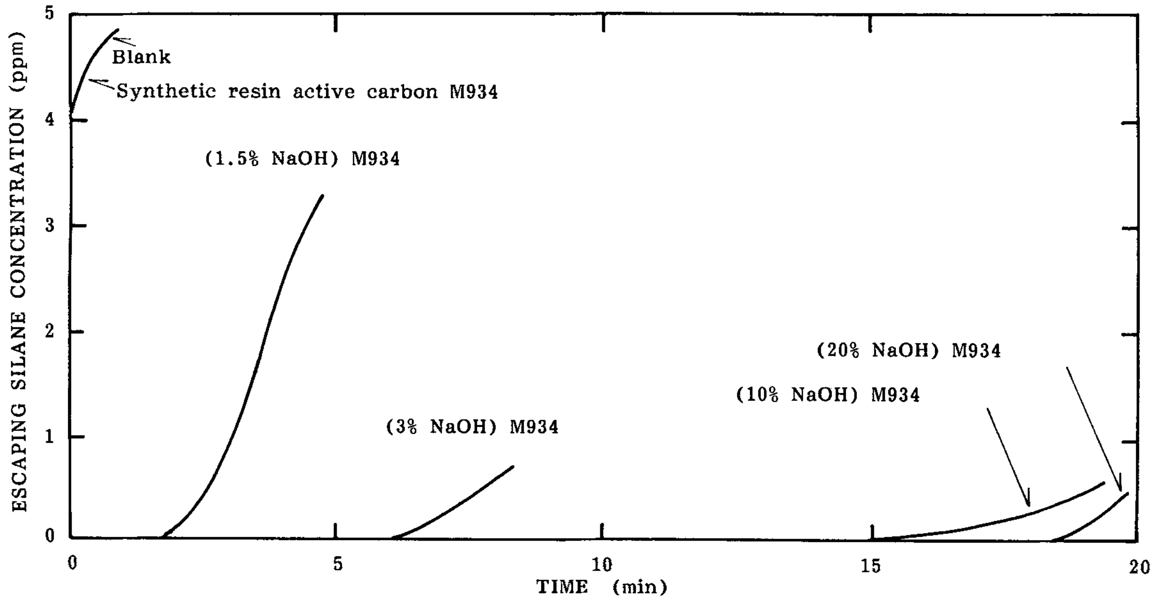

Figure 4 Breakthrough curves of silane test gas from sodium hydroxide-impregnated active-carbon beds. Silane: 5 ppm, 500 $cm^3 min^{-1}$; adsorbent: 300 mg.

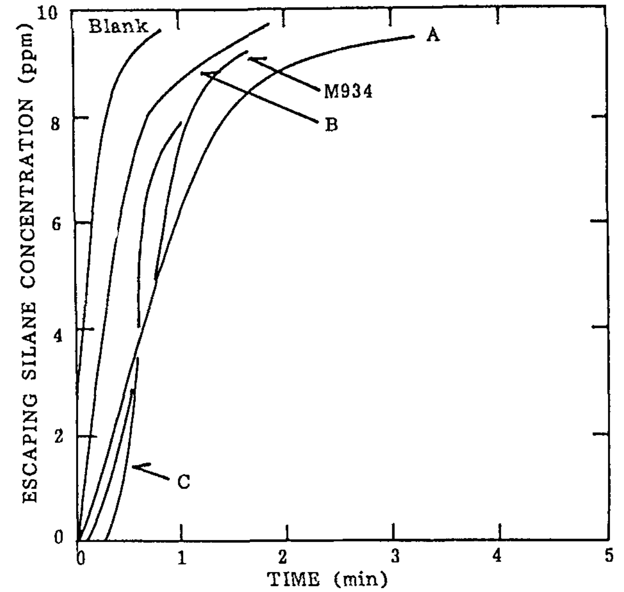

Figure 5 Breakthrough curves of silane test gas from adsorbent beds. Silane: 10 ppm, 270 $cm^3 min^{-1}$; adsorbent A: M934 impregnated with $HgCl_2 + NaCl$, 100 mg; adsorbent B: M145 impregnated with Na_2CO_3, 200 mg; adsorbent C: M934 impregnated with Na_2CO_3, 200 mg; M934: 200 mg.

The other chemicals, such as sodium carbonate and mercury(II) chloride, were less effective, as shown in Fig. 5.

Dichlorosilane

The synthetic-resin active carbon itself adsorbed dichlorosilane, but impregnation with sodium hydroxide increased the adsorption capacity. The breakthrough time of the NaOH-impregnated M915 (100 mg) was longer than 60 min for dichlorosilane test gas at 90.9 ppm drawn at 300 $cm^3 min^{-1}$, as shown in Fig. 6.

3.4 Desorption of the adsorbed gases from the adsorbents into solvents

Arsine

The synthetic-resin active carbon (200 mg of M915) which previously adsorbed arsine (0.5 ppm in nitrogen, 1.6 dm^3) was immersed in 10 cm^3 of 0.01 mol dm^{-3} nitric acid solution and treated at 80°C for 1 h, and the arsenic concentration in the supernatant was analysed by graphite furnace AA. The desorption efficiency of the adsorbed arsine into the supernatant was 94%. The desorption was improved by adopting a higher incubation temperature, as shown in Table 3. Arsine collected on the same active carbon was not effectively desorbed into basic solutions containing sodium hydroxide or ammonium hydroxide. Arsine collected on sodium hydroxide-impregnated M915 was treated with distilled water, which resulted in a low desorption of about 20%. When arsine was adsorbed by potassium

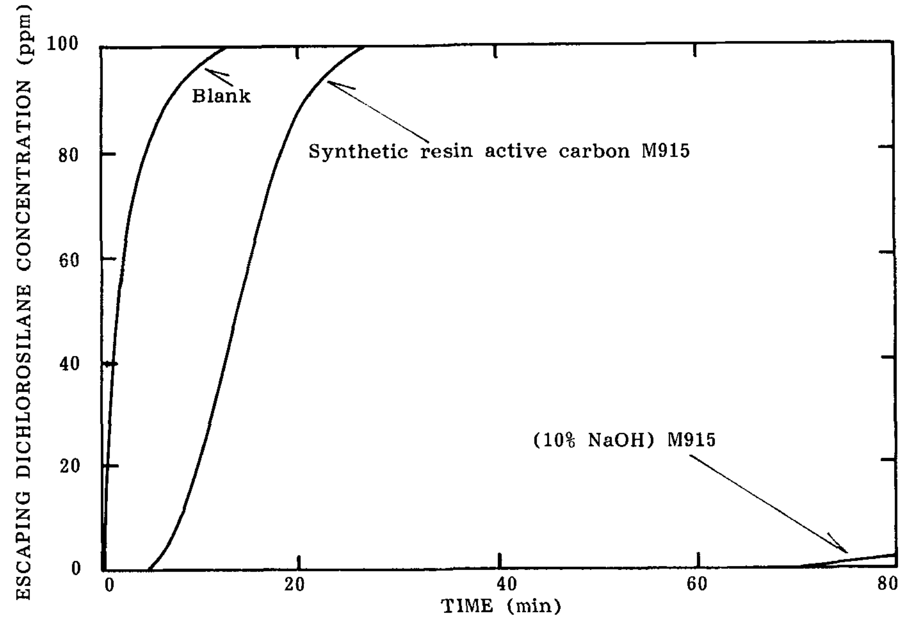

Figure 6 Breakthrough curves of dichlorosilane from adsorbent beds. Dichlorosilane: 90.9 ppm, 300 $cm^3 min^{-1}$; adsorbent: 100 mg.

Table 3 Desorption of arsenic and silicon from adsorbents

Adsorbent	Impregnant	Solvent	Treatment	Recovery[a] (%)
Arsine – synthetic-resin active carbon				
M915		HNO_3 (0.01 mol dm^{-3})	US/60 min	82.5
		HNO_3 (0.01 mol dm^{-3})	80°C/60 min	102.5
		NaOH (0.01 mol dm^{-3})	80°C/60 min	5.9
		NaOH (0.1 mol dm^{-3})	80°C/60 min	9.7
		NH_4OH (0.01 mol dm^{-3})	80°C/60 min	24
		NH_4OH (0.1 mol dm^{-3})	80°C/60 min	10.7
M915	NaOH (10%)	H_2O	US/60 min	20.5
Arsine – silica gel				
EB	$KMnO_4$(0.05%)	$NH_2OH \cdot HCl$(400 $\mu g\ cm^{-3}$)	RT	70.0
	$KMnO_4$(1%)	$NH_2OH \cdot HCl$(400 $\mu g\ cm^{-3}$)	RT	43.5
	$\begin{pmatrix} KMnO_4(1\%) \\ H_2SO_4(1\%) \end{pmatrix}$	H_2O	US/60 min	7.9
Silane – synthetic-resin active carbon				
M145	NaOH (10%)	H_2O	90°C/60 min	76
M145	NaOH (10%)	HNO_3 (6 mol dm^{-3})	90°C/60 min	43.5
M915	NaOH (20%)	H_2O	80°C/60 min	93
Dichlorosilane – synthetic-resin active carbon				
M145		NaOH (0.1 mol dm^{-3})	90°C/60 min	56.4
M145		HNO_3 (6 mol dm^{-3})	90°C/60 min	85.5
M145		Toluene	RT/60 min	0
M145	NaOH (10%)	H_2O	90°C/60 min	43.5

Abbreviation: US, ultrasonic vibration; RT, room temperature

[a] The values are the averages of six measurements.

The underlined values are the highest recovery attained from an adsorbent.

permanganate-impregnated silica gel and desorbed into hydroxylamine – hydrochloric acid solution, the desorption efficiency varied in the range from 70 to 43.5% depending on the hydroxylamine concentration. Excessive amounts of hydroxylamine resulted in a lower arsenic concentration in the supernatant.

Silane

When silane collected on sodium hydroxide-impregnated active carbon was treated in water at 80°C for 1 h, desorption of about 93% was attained. A nitric acid solution (6 mol dm^{-3}) was not effective for desorption of silicon from sodium hydroxide impregnated active carbon, as shown in Table 3.

Dichlorosilane

Dichlorosilane adsorbed on the active carbon, M145, was most effectively desorbed with a nitric acid solution (6 mol dm^{-3}) with desorption efficiency of 85.5%. Sodium hydroxide solution and toluene as the desorbing solvents were not effective. Dichlorosilane collected on sodium hydroxide-impregnated active carbon was desorbed into water at 90°C only with low efficiency of 43.5%.

4 DISCUSSION

Active carbon made from synthetic resin beads was proved useful for adsorption sampling of arsine, silane and dichlorosilane. Its impurity content was very small and it had useful adsorption capacities for arsine and dichlorosilane and was also able to carry sodium hydroxide for silane adsorption. Coconut-shell active carbon was not favourable for this purpose, because it was contaminated with arsenic and silicon at high concentrations which would interfere the determination of adsorbed arsine and silanes. Silica gels were not contaminated with arsenic, and were also useful as the sampling materials for arsine. The adsorption mechanisms of arsine, silane and dichlorosilane by active carbon and sodium hydroxide-impregnated active carbon were not investigated in this study. However, arsine and silane do not have strong polarity and have rather small molecular weights which are not favorable for physical adsorption. These properties may be the reason for weak adsorption of the gases on active carbon and silica gel. The effectiveness of sodium hydroxide in gas adsorption may be due partly to an increase of surface polarity and partly to an acceleration of the rate of oxidation of the gases. When they are adsorbed on the potassium permanganate-impregnated silica gel they are considered to be oxidized, and this mechanism may be predominantly effective for this adsorbent. The physical adsorption of dichlorosilane on active carbon was considered by analogy with that of dichloromethane on active carbon, but the adsorbed dichlorosilane was not desorbed into toluene. It was most effectively desorbed with a nitric acid solution. This suggests that dichlorosilane might be decomposed in the adsorbed state.

The low desorption efficiencies of arsenic and silicon into the solutions from the adsorbents which previously adsorbed arsine, silane and dichlorosilane, might be attributable partly to the formation of chemical bonding between the adsorbates and some components of the adsorbents and partly to sedimentation of the desorbed species in the solvents. The low desorption of arsenic from sodium hydroxide-impregnated active carbon might be due to the formation of less soluble hydroxides. Arsine adsorbed on potassium permanganate-impregnated silica gel might be reduced again with hydroxylamine to form volatile arsenic compounds like arsine in the desorbing solution.

The sensitivity of graphite furnace AA of arsenic and silicon was influenced by the elements coexisting in the sample solutions. The effect of nickel ions to intensify the absorbance of arsenic is well known, but the absorbance of arsenic was also intensified with potassium permanganate and weakened with sodium ions, chloride ions, hydroxylamine and ammonium ions. The absorbance of silicon was also intensified with nickel ions and weakened with sodium ions. These observations indicate that the amounts of arsenic or silicon in the sample solutions should be determined in comparison with the standards in the same matrix components.

5 CONCLUSION

This study showed that adsorption sampling of airborne arsine and dichlorosilane was possible using synthetic-resin active carbon, and that sampling of silane was possible with sodium hydroxide-impreganted synthetic-resin active carbon. The concentration of silane can be differentiated from that of dichlorosilane by drawing the sample air through an active carbon tube connected upward to a sodium hydroxide-impregnated active carbon packed tube. To prevent airborne particles being drawn into the adsorbent bed, a membrane filter should be placed on the inlet of the adsorbent tube with a suitable filter holder. The sampled gases can be dissolved with suitable solvents, i.e. arsine and dichlorosilane with nitric acid solutions and silane with water, and determined by graphite furnace AA. These methods will make field surveys of atmospheric contamination possible with satisfactory sensitivities to detect one-tenth of the PELs of these gases.

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