Silica gel adsorbents for sampling tube in work environment measurements and their extraction efficiency of alcohols

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Silica gel is commonly used as a sampling agent in small glass tube products for work environment measurements of organic solvent vapor, as established by the Industrial Safety and Health Act in Japan. However, to date there has been no national standard for sampling tube products, and the extraction efficiency of adsorbed organic solvent vapor from silica gel significantly affects the accuracy of measurement. Here, we have investigated the material properties of silica gel used in typical Japanese sampling tube products, and the effects on the efficiency as determined by the phase equilibrium method. This study focused particularly on specific surface area, porosity and grain diameter of silica gel specimens.

Key-words: Adsorbents, Extraction efficiency, Organic solvent, Phase equilibrium method, Sampling tube, Silica gel

1. Introduction

Measurement techniques of harmful organic solvent vapors are very important for improvement of work environments. Silica gel (SiO2·nH2O) is a typical sampling agent used in small glass tube products for work environment measurements of organic solvent vapor (particularly alcohols and other polar organic substances below approximately a few hundred ppm) in air as established by the Industrial Safety and Health Act in Japan. In such measurements, organic solvent vapors are collected by the sampling tube using a suction pump at a constant time and flow rate. The organic solvent components are then extracted from the silica gel by an extraction solvent, and the extraction liquid is analyzed by gas chromatography. Next, the organic vapor concentration in air is calculated from the result and collected volume of air. This method for measuring the organic vapor concentration in air is called “the solid collection method”. However, the extraction efficiency of the organic solvent components decreases depending on the types and concentration of the organic solvents, and this tendency influences the accuracy of results. Furthermore, from the viewpoint of material chemistry, understanding the relation between material properties of silica gel and organic solvent extraction efficiency is a significant issue. Until now, the details of this area were left unresolved. In this study, we have investigated properties of silica gel used in typical Japanese sampling tube products, and their effects on extraction efficiency as determined by the phase equilibrium method described later.

2. Experimental procedures

This study was performed using granular silica gel specimens derived from 5 types of commercially available Japanese sampling tube products purchased in 2014. In addition, we used 2 types of spherical silica gel products as a test reagent (small granule products dispensed by Kanto chemical Co., Inc. and Wako pure chemical industries, Ltd.) for reference samples.

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with a hydrogen flame ionization detector (FID), and C-R8A Chromatopac data processor for measurements. A capillary column SHIMADZU CBP1-S25-050 was used in the equipment, and each measurement was performed at a constant temperature of 323 K. Helium gas (≥99.999%) was used as the carrier gas for each measurement.

3. Results and discussion

Figure 1 shows the schematic diagrams of typical silica gel sampling tube products available in Japan, and the measurement results of the weight and size of silica gel layers in the sampling tube products are shown in Table 1. In Japan, until now, there has been no national unified standard for sampling tube products in work environment measurements. The sampling tube products have different inside and outside diameters (4–6 and 6–8 mm, respectively). Furthermore, they also have different lengths of glass body and weight of silica gel. The products were divided into 2 types, i.e., the products with main and backup silica gel layers [Fig. 1(a)], and those with a single silica gel layer [Fig. 1(b)] in the glass tube. In many cases, single layer type products are used for measurements of approximate known organic vapor concentrations in work places.

![Fig. 1. Schematic diagrams of typical silica gel sampling tube products. (a) Double layer type. (b) Single layer type.](image)

![Fig. 2. The representative images of silica gel specimens in this study at magnification ×40. (a) crushed type specimen D (b) spherical type specimen F. The scale is in common for the images (a) and (b).](image)

### Table 1. Weight and size of silica gel layer in the sampling tube products (described in Fig. 1) in this study

| SAMPLE | A | B | C | D | E |
|--------|---|---|---|---|---|
| Type   | Double layered | Double layered | Single layered | Double layered | Double layered |
| Product name | KOMYO No.801 | GASTEC No.252S | GASTEC No.252S2 | SIBATA | SIBATA |
| Number of samples | 5 | 5 | 5 | 5 | 6 |
| Outside diameter of tube/mm | 7.0 ± 0.0 | 7.0 ± 0.0 | 7.0 ± 0.0 | 8.0 ± 0.0 | 6.0 ± 0.0 |
| Inside diameter of tube/mm | 5.0 ± 0.0 | 5.0 ± 0.0 | 6.0 ± 0.0 | 6.0 ± 0.0 | 4.0 ± 0.1 |
| Silica gel bed thickness/mm | (1) 20.3 ± 0.4 | (1) 29.3 ± 0.4 | (1) 267 ± 0.4 | (1) 138 ± 0.2 | (1) 138 ± 0.2 |
| Silica gel bed weight/mg | (2) 7.1 ± 0.2 | (2) 14.2 ± 0.2 | (2) 12.6 ± 0.5 | (2) 6.8 ± 0.2 | (2) 6.8 ± 0.2 |
| Silica gel bed weight/mg | (1) 314.0 ± 6.3 | (1) 412.0 ± 2.7 | (1) 526.9 ± 11.7 | (1) 149.7 ± 2.3 | |
| Silica gel bed weight/mg | (2) 113.0 ± 4.8 | (2) 214.3 ± 2.1 | (2) 263.5 ± 7.4 | (2) 78.3 ± 1.2 | |
| Bulk density/g cm⁻³ | (1) 0.788 ± 0.014 | (1) 0.716 ± 0.013 | 0.721 ± 0.012 | (1) 0.698 ± 0.010 | (1) 0.848 ± 0.040 |
| Bulk density/g cm⁻³ | (2) 0.810 ± 0.012 | (2) 0.769 ± 0.010 | 0.740 ± 0.022 | (2) 0.740 ± 0.022 | (2) 0.898 ± 0.046 |

### Table 2. Porous properties, particle configuration and true densities of the silica gel specimens in this study

| SAMPLE | A | B | C | D | E | F | G |
|--------|---|---|---|---|---|---|---|
| Product | Sampling tube | Sampling tube | Sampling tube | Sampling tube | Sampling tube | Test reagent | Test reagent |
| Nₛ−BET specific surface area/m² g⁻¹ | 525 | 660 | 654 | 746 | 650 | 587 | 728 |
| Vₘₗₑₙ /cm³ g⁻¹ | 0.301 | 0.378 | 0.370 | 0.421 | 0.369 | 0.330 | 0.399 |
| Vₘₐₑₙ /cm³ g⁻¹ | 0.172 | 0.234 | 0.229 | 0.232 | 0.231 | 0.166 | 0.182 |
| Average pore width | 1.281 | 1.404 | 1.398 | 1.190 | 1.414 | 1.214 | 1.055 |
| by t-method or t-plot/mm | | | | | | | |
| Configuration of granules | Crushed | Crushed | Crushed | Crushed | Crushed | Spherical | Spherical |
| Year purchased | 2014 | 2014 | 2014 | 2014 | 2014 | 2015 | 2015 |
| Average diameter of granules/mm (N = 20) | 1.01 ± 0.03 | 0.98 ± 0.02 | 0.99 ± 0.03 | 0.99 ± 0.02 | 1.04 ± 0.02 | 1.56 ± 0.15 | 2.08 ± 0.04 |
| True density/g cm⁻³ | 1.961 ± 0.007 | 2.020 ± 0.006 | 2.025 ± 0.011 | 2.034 ± 0.008 | 2.001 ± 0.007 | 2.146 ± 0.015 | 2.196 ± 0.013 |
| N = 8 | N = 8 | N = 8 | N = 8 | N = 9 | N = 8 | N = 6 |

Nᵥₘₐₑₙ: micropore volume calculated by the MP method. Vₘₐₑₙ: mesopore volume calculated by the D-H method.
The porous properties, particle configuration and true densities of the silica gel specimens examined in this study are described in Table 2. The silica gel specimens A–E are crushed type silica gel taken from typical Japanese sampling tube products, and the specimens F and G are spherical type silica gel specimens which are test reagent products (Fig. 2). The granules of crushed type specimens have diameters in the vicinity of 1 mm. On the other hand, the granules of spherical type specimens have diameters of approximately 1.5–2.0 mm. The N$_2$–BET specific surface areas of the silica gel specimens are ranged from 525 to 746 m$^2$/g. These values were clearly lower than those of activated carbon used in Japanese sampling tube products$^{13}$ (approximately 970–1430 m$^2$/g). The values were also restricted in distribution as compared with those of activated carbon. Additionally, the results of X-ray fluorescence (XRF) analysis for the principal compositions of the silica gel specimens calculated by the FP (Fundamental Parameter) method,$^{20–22}$ which determines element composition of specimens from measured intensity of XRF and theoretical calculation, with assumed oxide compositions are described in Fig. 3. In the analysis and calculation, several light elements (atomic number $Z = 1–8, 10$) were excluded for clarity, and H$_2$O was outside the bounds of consideration. XRF analysis indicates that the crushed type specimens derived from sampling tube products have an extremely high content rate of Si $\geq 99.5$ mass %. On the other hand, the analysis also indicates that the spherical specimens F and G have several impurities in common (S, Ca and Fe), and their content rate is higher compared with the other

![Fig. 3. Results of XRF analysis for the principal compositions of the silica gel specimens calculated by the FP method with assumed oxide compositions. In the analysis and calculation, light elements (atomic number $Z = 1–8, 10$) were excluded.](image)

The diagrams show the pore size distributions and pore development in the mesoporous region (Fig. 4) and microporous region (Fig. 5) of the silica gel specimens calculated by the Dollimore–Heal (D–H) and MP methods. The data are presented in a logarithmic scale, with the pore size distribution plotted on a semilogarithmic graph.
crushed type specimens A–E. In addition, the XRF profiles of specimens B and C show very close resemblance.

The spherical specimens F and G have also high true density (Table 2) as compared with the crushed type specimens. From the results, some influence of shape forming in the manufacturing process on true density is expected, rather than influence of content rate of impurities. However, the details are unclear, and additional investigation is required.

Figures 4 and 5 show pore size distributions and pore development of the silica gel specimens in the mesoporous and microporous regions. The results show that the silica gel specimen has little correlation to pore size distribution. In other words, difference in specific surface area of the specimens is attributable to difference in degree of pore developments. In the figures, the profiles of specimens B and C in Fig. 4(a) are remarkably similar. Therefore, in comparison with the additional data described in Table 2, we concluded that the specimens B and C are almost equivalent.

In this study, extraction efficiencies of organic solvent components from the silica gel specimens were measured by phase equilibrium method\(^\text{(5,12)}\) (Fig. 6). In this method, test liquid solutions are prepared with a given amount of sampling agent, organic solvent of interest comparable to the collection amount and extraction solvent by one-time admixture. After the settling time (\(\geq 1\) h) and occasional shaking, the concentration of the organic solvent of interest in the test liquid is measured by gas chromatography. The phase equilibrium method has benefits in repeatability and simplicity as compared with measurement using rarefied organic vapors. Particularly, preparation and handling of rarefied organic vapors at a few ppm levels is difficult to achieve accuracy.

The relation between extraction efficiency and respective elements is indicated by the following theoretical formula\(^\text{(12)}\):

\[
D = \frac{1}{K \left( \frac{M_a}{M_s} \right) + 1} \tag{1}
\]

where:

\(D\): Extraction efficiency [dimensionless number]

\(K\): Equilibrium constant [dimensionless number]

\(M_a\): Weight of sampling agent [mg]

\(M_s\): Weight of extraction solvent [mg]

The extraction efficiency changes depending on the relative amounts of sampling agent and extraction solvent.\(^\text{(5,12)}\) From Eq. (1), the extraction efficiency can be increased significantly by maximum reduction of \(M_a\) or increase of \(M_s\). However, in the former case, reduction of \(M_a\) impairs the sampling of organic solvent vapor in the work environment. In the latter case, concentration of components of interest in the test solution for gas chromatography becomes extremely diluted. In both cases, analytical sensitivity of the measurement is markedly degraded, therefore leading to unfavorable conditions. In the present study, we standardized the amounts of silica gel and extraction solvent used for each measurement by referencing actual silica gel thin layers in sampling tube products (Table 1) in order to facilitate a suitable comparison of the measurement results.

Figure 7 shows the measurement results of extraction efficiencies of organic solvent components from the silica gel specimens. In the measurements, specimen B was omitted because specimens B and C were identical as previously noted.

In the figures, Figs. 7(a) and 7(b) show the results of cyclohexanol and Figs. 7(c) and 7(d) show the results of isopropyl alcohol. The extraction efficiencies have dependence on the types of organic solvent used respectively. In addition, the efficiencies are unstable in the approximate region of objective organic solvent concentration \(\leq 10\) ppm, and this instability was noticeable in the case of isopropyl alcohol. Similar instability was also confirmed in the previous experiments\(^\text{(5,14)}\) using activated carbon adsorbents, and clarification of the instability of extraction efficiency and the dependence on types of organic solvent needs further investigation.

Figures 7(a) and 7(c) show the results of silica gel specimens A, C and D. In the figures, several plots show extraction efficiencies \(> 1.00\) attributable to effects of volatilization of organic solvents or measurement precision of the gas chromatography system used in this study. Complete solution of the above experimental error is difficult, and data \(> 1.00\) shall be deemed to be almost 1.00.\(^\text{(7,13)}\)

However, other specimens E–G show evidently excessive values particularly in the case of cyclohexanol [Figs. 7(b) and 7(d)], and the specimens are inadequate from the viewpoint of accuracy. Additionally, the efficiencies indicate an ascending trend with decreasing concentration of cyclohexanol [Fig. 7(b)]. The specimens E–G have large grain diameters as compared with the rest of the silica gel specimens. The measurement results also show gradual degradation almost in the order of the specimens E, F and G [Fig. 7(b)]. This order also corresponds to that of their grain diameters (Table 2). In fact, silica gel adsorbents which have large grain diameter are likely to adsorb methanol as an extraction solvent. As a result, the extraction efficiency of the objective organic solvent component is overestimated. Silica gel adsorbents which have large grain diameter \(> 1\) mm are insufficient for high accuracy in work environment measurements.

On the other hand, the results of silica gel specimens A, C and D in Figs. 7(a) and 7(c) slightly show gradual improvement in order of the specimens A, C and D particularly in the region of 0.5E–1.0E. The order also corresponds to that of their specific surface area (Table 2). The result indicates that large specific surface area of silica gel has a favorable effect on extraction efficiency. The tendency of adsorbents is opposite of that of activated carbon adsorbents.\(^\text{(13,14)}\) The activated carbon specimens in the previous experiments were microporous carbon materials,
and excess pore development in the adsorbents seems to decrease extraction of the organic solvent components from micropores. In contrast, silica gel specimens in this study are mesoporous materials, and pore development in mesoporous regions contributes to the increase of specific surface area. The difference of pore volume in mesoporous regions between the specimen C and D is small (Table 2); however, ample pore development in the mesoporous region of silica gel specimens is expected to have a favorable effect on extraction efficiency in this study.

4. Conclusions

We have investigated the material properties of silica gel used in typical Japanese sampling tube products, and the effects on the efficiency as determined by the phase equilibrium method. Silica gel adsorbents which have large grain diameter are likely to adsorb methanol as an extraction solvent, and the extraction efficiency of the objective organic solvent component (cyclohexanol and isopentyl alcohol) is overestimated. As a result, silica gel adsorbents which have large grain diameter >1 mm are insufficient for high accuracy in work environment measurements. The result in this study indicates that large specific surface area of silica gel has a favorable effect on extraction efficiency, and ample pore development in the mesoporous region of silica gel is expected to have a favorable effect on the efficiency.

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