A new desorption method for removing organic solvents from activated carbon using surfactant

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Abstract: Objectives: A new desorption method was investigated, which does not require toxic organic solvents. Efficient desorption of organic solvents from activated carbon was achieved with an anionic surfactant solution, focusing on its washing and emulsion action.

Methods: Isopropyl alcohol (IPA) and methyl ethyl ketone (MEK) were used as test solvents. Lauryl benzene sulfonic acid sodium salt (LAS) and sodium dodecyl sulfate (SDS) were used as the surfactant. Activated carbon (100 mg) was placed in a vial and a predetermined amount of organic solvent was added. After leaving for about 24 h, a predetermined amount of the surfactant solution was added. After leaving for another 72 h, the vial was heated in an incubator at 60°C for a predetermined time. The organic vapor concentration was then determined with a flame ionization detector (FID)-gas chromatograph and the desorption efficiency was calculated.

Results: A high desorption efficiency was obtained with a 10% surfactant solution (LAS 8%, SDS 2%), 5 ml desorption solution, 60°C desorption temperature, and desorption time of over 24 h, and the desorption efficiency was 72% for IPA and 9% for MEK. Under identical conditions, the desorption efficiencies for another five organic solvents were investigated, which were 36%, 3%, 32%, 2%, and 3% for acetone, ethyl acetate, dichloromethane, toluene, and m-xylene, respectively. Conclusions: A combination of two anionic surfactants exhibited a relatively high desorption efficiency for IPA. For toluene, the desorption efficiency was low due to poor detergency and emulsification power.

Key words: Activated carbon, Desorption, Organic solvent, Surfactant

I. Introduction

The direct sampling method, solid adsorption method, and liquid absorption method are used for working environment measurements. Among these, the direct sampling method and solid adsorption method are widely used. The direct sampling method is used for collecting environmental air using a sampling bag and the sampled air is analyzed using a gas chromatograph. However, as the administrative levels in the working environment measurement have been reduced in recent years, the direct sampling method may not be applicable for some solvents. The solid adsorption method is used for measuring low concentrations of organic solvents. This involves collecting organic solvent vapors in a solid adsorbent by introducing environmental air with a pump into a glass tube packed with adsorbents, such as activated carbon or silica gel. This method can concentrate a target material by increasing the quantity of environmental air that can be sampled. However, for the analysis, it is necessary to separate the organic solvents by desorbing them from the adsorbent. The desorption method includes the solvent desorption method and thermal desorption method. The thermal desorption method involves heating the adsorbent in a tube to more than 200°C and analyzing the desorbed vapor using gas chromatography (GC). However, this method is rarely adopted for working environment measurement because it requires expensive equipment. The solvent desorption method involves extracting the adsorbed organic vapor from the activated carbon with a desorbing solvent and analyzing the solution using GC. This solvent extraction method is generally adopted by most measuring organizations because it does not require special equipment for desorption. The type of desorption solvent depends on target vapors and adsorbents, but car-
bon disulfide is used for many organic vapors adsorbed on activated carbon. Carbon disulfide has many advantages: Its desorption efficiency from activated carbon is high for many organic solvents and its sensitivity on an FID detector is quite low. On the other hand, carbon disulfide is extremely hazardous to humans and is reported to have caused peripheral neuropathy\(^6\)\(^7\). The recommended values for both TLV-TWA of ACGIH and Occupational Exposure Limits of the Japan Society for Occupational Health are 1 ppm. In addition, carbon disulfide is cited as a Class 1 organic solvent in an Ordinance on the Prevention of Organic Solvent Poisoning in Japan, which also recommends that the occupational exposure limit in working environments should be 1 ppm.

As shown above, although its hazardousness for humans is very high, carbon disulfide is routinely used as a desorption solvent in the analysis because of its excellent characteristics. Hence, workers conducting such analyses would be exposed to carbon disulfide. It is thus essential to protect the health of such workers in future over a long time, especially as the health effects of long-term low-concentration exposure to chemicals have become apparent.

If there was a method that could extract materials from a sampling agent without using a harmful organic solvent, such as carbon disulfide, then this would be extremely beneficial with respect to protecting the health of the analysis workers. Therefore, this study aims to examine a new desorption solvent to replace carbon disulfide, focusing on surfactants that have both hydrophilic and lipophilic groups. Surfactants are used in detergents for cloth washing because a lipophilic material can apparently dissolve in a hydrophilic solution\(^8\). By applying this property of the surfactant, organic solvents adsorbed on the activated carbon can be desorbed. This study aims to determine suitable conditions for the effective desorption of an organic solvent adsorbed on coconut-shell-activated carbon using an anionic surfactant solution, considering the effect of surfactant concentrations, amount of desorption liquid, desorption temperature, and desorption time on the desorption efficiency of organic solvents.

II. Method

1. Organic solvent addition to activated carbon

The coconut-shell-activated carbon (100 mg) derived from a charcoal tube (SIBATA SCIENTIFIC TECHNOLOGY LTD., Charcoal Tubes, Standard Type, Tokyo, Japan) was put in a screw vial with 10-ml headspace. Then, 10 μl of the organic solvent solution diluted with distilled water was added and the cap on the vial was closed. Then, after shaking lightly, the vial was left in an incubator (PCI-101, ASONE) at 25°C for 24 h.

Approximately one-tenth of the administrative level of the organic solvent in 1.5 l air was added to a charcoal tube. The organic solvents used in the examination of desorption conditions were isopropyl alcohol (IPA) and methyl ethyl ketone (MEK) (Wako Pure Chemical Industries, Ltd., a special grade reagent, Osaka, Japan). These were diluted with distilled water (KANTO KAGAKU, distilled water for HPLC, Tokyo, Japan) before use.

2. Desorption

A predetermined quantity of an organic solvent was adsorbed in a vial by an activated carbon and the surfactant solution was added. The organic solvent that existed in the gas phase was so small that it was negligible as compared with that in the solid phase when the adsorption equilibrium was established. In fact, we checked an adsorption efficiency using IPA, MEK, and toluene and confirmed that the adsorption efficiency was approximately 100%. After capping, the vial was shaken lightly. Thereafter, the vial was put into an incubator at a predetermined temperature and left for a scheduled time. Then, the vial was put into an incubator at 60°C and left for approximately 1 h. Then, 250 μl gas from the headspace of the vial was extracted with a gas-tight syringe and injected into a gas chromatograph equipped with an FID (GC-17A, SHIMADZU, GC). Analytical conditions of the GC were as follows: Injection port temperature: 200°C, column oven temperature: 60°C, and detector temperature: 220°C; column: G-column (G-205, 2 μm, column size: 1.2 mm I.D. ×40 m, Chemicals Evaluation and Research Institute, Japan); and carrier gas: nitrogen at a flow rate of 20 ml/min. The coefficient of variation of measured values was confirmed by the analysis and was less than 5%. The desorption efficiency was calculated from the following equation.

\[
\text{Desorption efficiency (\%)} = \left( \frac{\text{Area value of vial with activated carbon}}{\text{Area value of vial without activated carbon}} \right) \times 100 - (1)
\]

In addition, the area level of the solvent in the gas phase of the vial without activated carbon was determined as follows. First, the surfactant solution was added in the vial. Then, the organic solvent solution was injected into the vial in the same amount in which the activated carbon was added. After keeping in the incubator at 25°C for 24 h at a predetermined desorption temperature for a predetermined time, analysis was conducted.

3. Desorption solution

Two anion-based surfactants, dodecyl benzene sulfonic acid sodium (Tokyo Chemical Industry Co., soft model, LAS) and sodium dodecyl sulfate (Wako Pure Chemical Industries, first-grade reagent, SDS) were combined as a mixed surfactant. The solution concentration ratio of LAS:SDS was fixed at 8:2, and 1%, 5%, 10%, and 20% solutions were prepared as shown in Table 1. Distilled
water was used to dilute the organic solvent.

The calculated desorption efficiencies were compared using the Steel-Dwass method.

4. Quantity of desorption liquid

For 1 ml and 5 ml of the 10% surfactant solution, the desorption efficiencies were calculated from equation (1) and compared.

5. Desorption temperature

The temperatures at which desorption occurred were 25°C, that is, the standard room temperature of the work environment, and 60°C, which was the headspace temperature at the time of analysis. A 10% surfactant solution was used for desorption. 5 ml solution was added at the time of desorption, and the desorption efficiency at each temperature was calculated.

6. Desorption time

The effect of desorption time on the desorption efficiency of IPA was studied using 5 ml of the 10% surfactant solution.

A vial containing 10 μl of the IPA solution diluted with distilled water 100 times and 100 mg of activated carbon was left at 25°C for 24 h. Then, the desorption liquid was added and the vial was put in an incubator at 60°C. The desorption efficiency was determined 1, 2, 3, 6, 24, 48, or 72 h later.

7. Desorption efficiency for various organic solvents

The desorption efficiency of seven organic solvents was determined using 5 ml of the 10% surfactant solution and a desorption temperature of 60°C for 24 h. In addition to IPA and MEK, ethyl acetate, acetone, and dichloromethane were tested. All solvents were diluted with distilled water (Kanto Chemical, HPLC) before use. For toluene and m-xylene, a quality of the water standard material (Kanto Chemical, 1 mg/ml with methanol) was used.

III. Results

1. Surfactant concentrations

The change in the desorption efficiency with surfactant concentration is shown in Fig. 1. The desorption efficiency for IPA is 71% in 1% solution, 73% in 5% solution, 80% in 10% solution, and 79% in 20% solution. On the other hand, the desorption efficiency of MEK is 5.7% in 1% solution, 9.9% in 5% solution, 13% in 10% solution, and 14% in 20% solution.

A multiple comparison test was used to compare the desorption efficiencies. The desorption efficiency of the 1% solution is significantly lower than that of the other concentrations for MEK. The desorption efficiency for the 5% solution is not significantly different from that of the 10% solution, but a significant difference is found for the desorption efficiency of the 20% solution. There is no difference in the desorption efficiency between the 10% and 20% solutions.

**Table 1.** Composition of surfactants (mg/ml)

| Surfactant | 1%  | 5%  | 10% | 20% |
|------------|-----|-----|-----|-----|
| SDS        | 0.4 | 2.0 | 4.0 | 8.0 |
| LAS        | 2.6 | 12.9| 25.8| 51.6|

![Desorption Efficiency Graph](image_url)

**Fig. 1.** Effect of surfactant solution concentration on desorption efficiency. 1%: 0.8% LAS and 0.2% SDS; 5%: 1.6% LAS and 0.4% SDS; 10%: 8% LAS and 2% SDS; and 20%: 16% LAS and 4% SDS in desorption solutions. (**p<0.01, *p<0.05)**
2. Quantity of desorption liquid
The effect of the quantity of surfactant solution on the desorption efficiency is shown in Fig. 2. The desorption efficiency for IPA is 55% with 1 mL solution and 82% with 5 mL solution. For MEK, it is 2.2% with 1 mL solution and 8.7% with 5 mL solution. The desorption efficiency with the 5 mL solution is higher than that with the 1 mL solution for both IPA and MEK.

3. Desorption temperature
The desorption efficiencies at 25°C and 60°C are shown in Fig. 3. The desorption efficiencies at 60°C are 75% for IPA and 20% for MEK. On the other hand, the desorption efficiencies at 25°C are 44% for IPA and 8% for MEK.

4. Desorption time
The effect of desorption time on the desorption efficiency of IPA is shown in Fig. 4. The desorption efficiencies are 24%, 38%, 48%, 69%, 87%, 87%, and 90% after 1, 2, 3, 6, 24, 48, and 72 h, respectively. The desorption efficiency increases with time up to 24 h, but reaches a plateau at this point, with only a very small increase between 24 and 72 h.

5. Desorption efficiency for seven solvents
The desorption efficiencies for seven organic solvents are shown in Table 2. The experimental conditions are 5 mL of the 10% surfactant solution and a desorption temperature of 60°C for 24 h. The desorption efficiencies of the organic solvents are 3%, 72%, 9%, 3%, 32%, 2%, and 3% for acetone, IPA, MEK, ethyl acetate, dichlorometh-
Fig. 4. Desorption efficiency for IPA as function of time.

Table 2. Desorption efficiency of organic solvents with the surfactant solution

| Organic solvent | Desorption efficiency (%) | Octanol/Water partition coefficient |
|-----------------|---------------------------|-----------------------------------|
| Acetone         | 36                        | -0.24                             |
| IPA             | 72                        | 0.05                              |
| MEK             | 9                         | 0.29                              |
| Ethyl acetate   | 3                         | 0.73                              |
| Dichloromethane | 32                        | 1.25                              |
| Toluene         | 2                         | 2.73                              |
| m-xylene        | 3                         | 2.77                              |

Condition for desorption was 5 ml of 10% surfactant solution and desorption temperature of 60°C for 24 h.

ane, toluene, and m-xylene, respectively.

IV. Discussion

In this study, the effects of desorption conditions, that is, the surfactant concentrations, quantity of desorption liquid, desorption temperature, and desorption time, on the desorption efficiencies of the organic solvents from the coconut-shell-activated carbon were investigated.

As shown in Fig. 1, the desorption efficiency of IPA is not affected by the surfactant concentrations; however, in MEK, the desorption efficiency increases when the surfactant concentrations are increased to 10%. Both the detergency and solubilization power of the surfactant may contribute to the desorption of the organic solvent from the activated carbon. The detergency increases up to the critical micelle concentration (cmc) of the surfactant, but when it reaches the cmc\(^6\), it does not change even if the surfactant concentration rises. On the other hand, the solubilization power begins to rise from a point beyond the cmc\(^6\). The cmc is the concentration of surfactant molecules at which molecular aggregates (micelles) are formed. The desorbed organic solvent solubilizes in a solution as well as an oil at the time of general washing\(^6\).

The cms of the two surfactants used in this study are 1.2 mM for LAS and 8 mM for SDS. Thus, even the lowest surfactant concentrations used in this experiment, that is, 1%, exceed the cmc. Therefore, the reason why the desorption efficiency increases with the surfactant concentration for MEK is improvement in the solubilization power rather than that in the detergency. The results shown in Fig. 2 also support this explanation. Fig. 2 shows the difference in the desorption efficiency for IPA and MEK when the quantity of desorption solution is 1 ml and 5 ml and a 10% surfactant solution is used. In both solvents, the desorption efficiency is higher when the quantity of desorption liquid is 5 ml. This may be because the amount of solvent that can be desorbed increases due to an increase in the volume of the solution, even when the concentration of the desorption solution is the same. However, no improvement in the desorption efficiency is found when the surfactant concentration is increased to more than 10%. In addition, when the surfactant concentration is 20%, the viscosity is so high that it is difficult to
add a fixed quantity of the surfactant into a vial. For IPA, the desorption efficiency does not appear to be affected by the surfactant concentration of the desorption solution but is affected by the surfactant concentration with MEK. This is because the anionic surfactant used in this experiment has comparatively high hydrophilicity; therefore, a hydrophilic organic solvent can easily be suspended in the desorption solution. The hydrophilicity of IPA is relatively high, according to the octanol/water partition coefficient shown in Table 2. Therefore, IPA is easily suspended in the surfactant solution. In addition, because IPA dissolves easily in water, a constant desorption efficiency is shown, which is not dependent on the surfactant concentration. On the other hand, because the hydrophilicity of MEK is lower than IPA, the desorption efficiency depends on the number of micelles in the solution; thus, the desorption efficiency is affected by the surfactant concentration. This result shows that desorption with a high concentration of surfactant solution is desirable for the desorption of hydrophobic organic solvents.

However, the most suitable concentration of the surfactant for the desorption solution in this study is 10%, because the desorption efficiency of the 10% and 20% solutions does not differ significantly for both IPA and MEK.

Fig. 3 shows the desorption efficiency of IPA and MEK at 25°C and 60°C for the surfactant concentrations of 10%. The desorption efficiency at 60°C is higher than that at 25°C for both IPA and MEK. This difference may be caused by a reduction in the surface tension of water at a higher temperature, rather than by the effect of the surfactant, and the adsorption equilibrium between activated carbon and the desorption solution changes with temperature, allowing more organic solvent to dissolve in the solution.

Fig. 4 shows changes in the desorption efficiency at different desorption times for IPA when a 10% surfactant concentration is used. The desorption efficiency increases with the desorption time up to 24 h, but there is no significant improvement in the desorption efficiency beyond this time. This result shows that at least 24 h are needed for the desorption of organic solvent from activated carbon when this surfactant combination is used as a desorption solution. The reason why an improvement in the desorption efficiency is observed up to 24 h is that time is necessary for a surfactant to penetrate from the surface to the pores of activated carbon. Activated carbon contains macropores, mesopores, and micropores. In general, the coconut-shell-activated carbon has many micropores. The diameter of a micropore is less than 2 nm, and therefore, sometime is required for the solution to penetrate it. When the solution penetrates the micropore, the organic solvent is desorbed. There is no change in the desorption efficiency thereafter. For the conventional desorption method using carbon disulfide, analysis is conducted 1 to 2 h after the desorbed is added to the activated carbon. Therefore, the desorption time of 24 h with the surfactant is much longer than that for the conventional method; hence, shortening of the desorption time is necessary.

As described above, in the case of desorption of organic solvents from activated carbon using the surfactant solution, many factors, such as surfactant concentration, quantity of desorption liquid, desorption temperature, and desorption time, affect the desorption efficiency. As shown in Table 2, the desorption efficiency of IPA is relatively high, but for practical use, a desorption efficiency of more than 90% is desirable, and therefore, an improvement in the desorption efficiency is necessary. To build on this result, further investigations should lead to shortening of the desorption time and improvement in the desorption efficiency. For this improvement in the solubilization and emulsification power of the desorption solution is needed. Anionic surfactant generally provides stronger solubilization and emulsification power than anionic surfactant(10). In addition, in the case of general washing, a builder, such as zeolite or sodium carbonate, which affects the micelle formation of surfactants, is added to the general water washing system(11,12). Using this method, the desorption efficiency can be improved.

In this study, we performed only one-tenth of the administrative level. However, we should examine different concentration ranges, that is, 1/2, 1, and 2 times of the administrative levels for applying actual working environment.

Conclusion

Surfactant concentrations, quantity of desorption liquid, desorption temperature, and desorption time affect the efficiency for the desorption of organic solvents from activated carbon using a surfactant.

Acknowledgments: This work was supported by JSPS KAKENHI, Grant Number 26860449.

Conflicts of Interest: The authors have no conflicts of interest to declare.

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