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Fundamental Study on the Production of Ultrapure Water. VI. Leachables from Strong Base Anion Exchange Resins.

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A study was made of the profiles of leachables from typical strong base anion exchange resins (SBAER, three gel and two porous types, OH form) widely used for producing ultrapure water. The leaching profiles were investigated by soaking SBAERs into purified water of less than 100 $\mu\text{gC/L}$ of total organic carbon (TOC) previously purged with nitrogen gas at 50°C.

The TOC values leaching from SBAERs were 1.4×10^{-1} to 3.0 mgC/h per dried resin of liter wet resin. The major TOC component was trimethylamine (about 50 % or over of the TOC values) produced by decomposition of the functional groups. The high molecular weight (MW) leachables ranged from above five hundred to less than ten thousand and contained components of MW 2,200, 4,000 and 5,900 as polystyrene sulfonates as determined by gel filtration chromatography in each experiment. There were three unknown prime substances in the low MW leachable components according to reverse phase chromatography (RPC). The chemical structures of the substances were determined based on the similarity of RPC results for leachables from SBAERs and strong acid cation exchange resins (SACER).

1 Introduction

Recently there has been an increasing demand for ultrapure water in the advanced and sophisticated industries such as those of semiconductor manufacturing, atomic power generation, pharmaceutical and medical-related industries^{1)~3)}. Removal of trace TOC present in the ultrapure wafer is becoming a key concern in such industries because TOC relates to bacterial proliferation and decrease of the wafer yield^{4),5)}. An ion exchange resin (IER) is an essential material to produce pure or ultrapure water by eliminating ions in water⁶⁾. Users in the advanced industries would like to use IER at elevated temperature to treat condensate water and to control bacterial growth. There is an annoying problem as trace leachables from IERs known as TOC throw in use or during storage^{7)~9)}. The trace leachables were substantially no problem in the conventional pure water production. What are the substances and how is the leaching profile have become a matter of great concern in the ultrapure water produc-

tion. There are information on the degradation and release of the functional groups on IERs^{10)~12)}. But few studies have been reported on the profile of leachables about SACERs in terms of the MW information and the identification^{14)~16)}. The components of the leachables from SBAERs, however, have scarcely been revealed, except they contain trimethylamine and methyl alcohol which are the degradation products of the functional groups and compounds with benzene ring of less than MW 1,000^{17),18)}.

In this study, the leaching rate and the components of leachables from SBAERs were investigated by soaking the resins in purified water at elevated temperature (50°C) prior to their removal. Measurements of the leachables were made by TOC analysis, gel filtration chromatography (GFC) and reverse phase chromatography (RPC).

2 Experimental

2.1 Materials

2.1.1 IER

Five commercially available SBAERs (A'-E') with crosslinked polystyrene matrix were tested. The resins have quarternary ammonium functional groups. These are typical resins for water treatment use and obtained from leading makers such as Tokyo Organic Chemical Industries Co., Ltd. (Amberlite), Mitsubishi Chemical Industries, Co., Ltd. (Diaion), Dow Chemical Co., Ltd. (Dowex), Bayer Co., Ltd. (Lewatit), and Rohm and Haas Co., Ltd. (Duolite). The brand-name of each resin is concealed because the key concern of this study is not to discuss the comparative merits of the resins on performance in purification of water. The resin A' and B' are

porous types, and C', D', and E' are gel ones. Pre-treatment and general properties of the resins are given in **Fig.-1** and **Table-1**, respectively. Weight capacity of resin C' and volume capacity of resins A' and B' were about 10 % lower than the other's.

2·1·2 Purified water

The same pure water as one used in the previous paper¹⁵⁾.

2·1·3 Reagent

Polystyrene sulfonate, MW 1,800, 8,000 38,180, 114,400, 400,000 (Gaschro Industry Co., Ltd.) and *p*-ethylbenzenesulfonic acid (Tokyo Kasei Co., Ltd.) were used to make the

Fig.-1 Pretreatment of SBAER.

Table-1 General properties of SBAER.

Resin	Moisture holding capacity (%)	Weight capacity (meq/g)	Volume capacity (meq/mL)	Density (g/L)	Effective size (mm)
SBAER					
A'	58.0	4.18	1.21	690	0.48
B'	58.7	4.26	1.21	690	0.50
C'	50.5	3.80	1.32	700	0.55
D'	46.0	4.11	1.35	678	0.55
E'	50.0	4.15	1.35	651	0.47

As salt form.

Fig.-2 Calibration curve of polystyrene sulfonate.

MW fitting curve for GFC analysis. The molecular fitting curve is shown in Fig.-2. Anhydrous sodium sulfate for fluorescence analysis and acetonitrile for HPLC were used to prepare the eluent for GFC. Acetonitrile was also utilized for the eluent of RPC analysis.

2.2 Procedure

2.2.1 Analysis of leachables from SBAER

1) Each pre-treated SBAER was put into a glass column and backwashed again using ten bed volumes of the purified water.

2) Then, the resin (50 mL) was put in a 250 mL of volumetric flask and the purified water which had been purged with nitrogen gas was messed up to the mark.

3) The flask was kept at 50°C with gentle stirring.

4) TOC and pH of the supernatant were periodically monitored. Trimethylamine (TMA) and methanol (MeOH) were determined by the absolute calibration method with gas chromatography (GC).

5) After 100d, the solution in the flask was filtered with a 0.22 μ m membrane filter (Millipore Industries Co., Ltd.)

6) MW distribution for the leachables was obtained by GFC and the low MW components in the leachables were analyzed by RPC.

2.3 Analytical equipment and conditions

TOC : TOC-10B (Shimadzu Co., Ltd.)

GC : GC-8A (Shimadzu Co., Ltd.)

Detector, FID 100°C

Column Amipack, 3 m glass column for TMA

HPLC : HLC-803D (Tosoh Co., Ltd.)

GFC : Detector, SPD-6A (Shimadzu Co., Ltd.)

UV 210 nm

Column, PW_{XL} 4,000 (i. d. 7.5 mm $\times$ h. 300 mm) + PW_{XL} 2,500 (i. d. 7.5 mm $\times$ h. 300 mm)

(Tosoh Co., Ltd.)

Eluent, 0.2 M Na₂SO₄ + 10 % acetonitrile

PRC : Detector, SPD-6A (Shimadzu Co., Ltd.)

UV 210 nm

Column, Silica ODS-80T_M (i. d. 4.6 mm $\times$ h. 150 mm)

(Tosoh Co., Ltd.)

Eluent, 45 % acetonitrile

Fraction collector : SF-16OK (Toyo Seisakusho Co., Ltd.)

3 Results and Discussion

Fig.-3 shows the change of TOC in the mixed solution of each SBAER and the purified water at 50°C. The general properties for the SBAERs after 100 d soaking were substantially the same as the initial ones given in Table-1. The TOC increased with soaking time. The TOC leaching rate was given in Table-2. The rates were $1.4 \times 10^{-1} \sim 3.0$ mgC/(h.L-dry resin). These values were much larger than the ones obtained from SACERs ($2.8 \times 10^{-2} \sim 1.1$ mgC/(h.L-dry resin)¹⁵⁾. As to the reason of the difference in the TOC leaching rates between SBAER and SACER, we reason it out later from the viewpoints of the decomposition mechanisms of IERs and the leaching mechanism of the leachables. The difference in the TOC leaching rates between gel type resins (C', D', E') and porous type ones (A', B') was not clear. The rate for resin E' was the smallest in the five. E' was obtained in the regenerated mixture with SACER of one to one

Fig.-3 Change of TOC in the mixed solution of SBAER and purified water at 50°C.

Table-2 TOC leaching rate of SBAER.

Resin	TOC ^{a)} mgC/L	TOC leaching rate mgC/(h·L-dry resin)
A'	107	3.0
B'	43.5	1.2
C'	77.7	2.2
D'	18.6	5.2×10^{-1}
E'	5.1	1.4×10^{-1}

a) TOC in the solution after 7 d soaking.

by volume. It is probable that most leachables with positive charge leaching out from resin E' must have been adsorbed on the paired SACER (H form) with negative charge in the mixed state. And also high MW leachables like a polystyrenesulfonic acid with negative charge from the paired SACER, which must have been adsorbed on resin E' in the mixed state, restrain the release of the leachables with positive charge from resin E' as shown in the following test. Twenty-five milliliters of resin C' (resin volume is one half in Section 2·2·1) adsorbed polystyrenesulfonic acid of MW 4,000 with saturated amount was soaked into the purified water at 50°C. The TOC value of the supernatant was 17.7 mgC/L (15% decrease), compared to the value (20.9 mgC/L) for the non-treated resin C' after one week.

Fig. -4 presents the change of pH in the mixed solution of each SBAER and the purified water at 50°C. The pH of the solution became strongly basic with soaking time. There was a relation between the amount of TOC and the pH of the solution. It seemed the larger TOC gave the higher pH. TMA and MeOH in the solution after 100d soaking were determined by GC with reference to the Hofmann degradation¹⁰⁾. **Table-3** shows the ratio of TMA, MeOH, and the other

Fig. -4 Change of pH in the mixed solution of SBAER and purified water at 50°C.**Table-3** Ratio of trimethylamine (TMA), methanol (MeOH), and unknown component to TOC from SBAER at 50°C after 100 d soaking.

SBAER	TOC (mgC/L-resin)	TMA (%)	MeOH (%)	Unknown component (%)
A'	1934	70.5	1.1	28.4
B'	1045	57.4	2.3	40.3
C'	904	57.1	3.4	39.5
D'	626	45.8	3.4	50.8
E'	471	72.0	6.6	21.4

component to the values of TOC released out of SBAERs after 100 d soaking at 50°C. It was found that TMA occupied 45.8 to 72.0 % of the TOC and was the dominant component in the leachables. MeOH existed in far less percentage than TMA. The unknown component was about 20 to 50 % in overall TOC in the leachables. Therefore, the main mechanism to release TOC from SBAER was concluded to depend on the following formula (i) issued on the decomposition of the functional groups in SBAER¹⁰⁾⁻¹²⁾.

Where R stands for the crosslinked polystyrene matrix. It can be considered that the TOC leaching rate from each SBAER in **Fig. -3** was dependent on the leaching rate of TMA formed by the decomposition of the functional groups. Consequently in SBAER, there was almost no difference in the TOC leaching rates between gel type resins and porous ones as the TOC leaching rate depended mainly on the decomposition of the functional groups. From the standpoint of the bond energy, it turns out that the decomposition of the functional groups occurred more easily than the one of the resin matrix relevant to the unknown leachable components because the decomposition of the functional group is due to the cleavage of C-N bond (305 kJ/mol), and the decomposition of the resin matrix is caused by the cleavage of C-C bond (347 kJ/mol) of at least over one¹⁹⁾. The TOC leaching rate from each SBAER showed much larger value than the one from each SACER paired except for resin D' as given in **Table-2** and **3** compared to our previous

results for resin D⁽⁵⁾.

Then, the profiles for the leachable components based on the degradation of the resin matrix except for the decomposition products of the functional sites was made clear. **Fig. -5** illustrated GFC chromatograms of the leachables from SBAERs after 100 d soaking at 50°C. The leachable solutions were diluted to about 4.5 times with the purified water and analyzed. The MW distribution for the leachables ranged from above 500 to less than 10,000 as polystyrene sulfonates. Three components of MW 2,200, 4,000, and 5,900 existed in common as high MW leachable components. The content of each component in the high MW components was different in each SBAER. The prime MW values of the leachable components from SBAERs appear to be larger than the ones from SACERs⁽⁵⁾. It is probable that this is due to the difference of the divinylbenzene (DVB, crosslinker) content in resins. The DVB content for SBAER is ordinary much lower than SACER's⁽²⁰⁾. The lower crosslinker content gives the longer uncrosslinked polystyrene and the longer linear polystyrene chains in between crosslinked polystyrene chains during polymerization process if there is no significant difference in the polymerization conditions for SBAER and SACER. After function-

Fig. -5 GFC chromatograms of leachables from resin A' - E' after 100 d soaking at 50°C.

alization of the crosslinked polystyrene beads prepared, the long uncrosslinked functionalized polystyrenes which must be entangled in the resin matrix and the long liner functionalized polystyrene chains are released out from the resin inside by the crosslinked polystyrene networks

Fig. -6 RPC chromatograms of leachables from resin A' - E' after 100 d soaking at 50°C.

are partly cut as explained in the previous paper¹⁶⁾. Fig. -6 represents the RPC chromatograms of the leachables from SBAERs after 100 d soaking at 50°C. There were three dominant decomposition products with retention times (RT) of 2.2, 3.4, and 5.4 min in every RPC chromatogram. These RPC chromatograms were similar to the ones for the leachables from SACER^{15), 16)}. As is known, RPC is a very useful tool to separate low MW organic substances' mixture into each component by the difference of polarity. The RPC technique is also available to identify aromatic compounds by the retention times for the known substances. We have already identified the leachable components from SACERs and found out there were *p*-sulfobenzoic acid (RT=3.6 min) and *p*-hydroxybenzenesulfonic acid (RT=4.4 min) in the leachables¹⁵⁾. Raw materials, the basic polymerization method, and the decomposition mechanism of the resin matrix are almost the same between SACER and SBAER except for the difference of the functional groups. Therefore, it should be expected that there are similar substances in the unknown leachable components from SBAERs to the detected materials in the leachables from SACERs as shown below.

According to the latest study on the prediction and identification of leachables from SACERs by the oxidative stress procedure using hydrogen peroxide (30 %) done by Stahlkush *et al.*^{20), 21)}, *p*-hydroxybenzenesulfonic acid and *p*-sulfobenzoic acid were formed by the degradation of the polymeric leachables and identified by ion-pair reversed-phase chromatography. It is reasonable to predict that the polymeric leachables and the monomeric components like stated above were formed in SBAERs by small amounts of oxidative materials in water as well as in hydrated water inside the resins. We are going to confirm the expected substances by using a LC-MS techni-

que.

4 Conclusions

Based on the results of this study on the profile of the leachables from SBAERs at 50°C, the following conclusions were drawn.

1) The TOC release rates from SBAERs used were from 1.4×10^{-1} to 3.0 mgC/h per dried resin of a liter wet resin in purified water at 50°C. The values were larger than the ones from SACERs.

2) Trimethylamine which is a decomposition product of the functional groups in SBAER occupied 45.8~72.0 % of the TOC leached from SBAERs and its leaching rate was influenced the TOC leaching rate from SBAERs.

3) The adsorption of polyelectrolytes like a polystyrene sulfonate on the surface of SBAER decreased the TOC leaching rate from SBAER.

4) The high MW components in the leachables were in the M. W. range of above 500 to less than 10,000 as polystyrene sulfonates', and the common prime components were MW 2,200, 4,000 and 5,900.

5) As low MW leachable components except for trimethylamine and methanol, substances of the RT of 2.2, 3.4 and 5.4 min were detected in common by RPC.

6) Through the similarity of RPC chromatograms for the leachables from SBAERs and SACERs, and the decomposition mechanism of the resin matrix, the existence of the following two leachable components were expected.

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超純水製造に関する基礎的研究 (第6報) 強塩基性陰イオン交換樹脂からの溶出物

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本研究では純水製造に用いられる代表的強塩基性陰イオン交換樹脂 (SBAER, ゲル型 3 種と多孔性 2 種) からの微量溶出物について調べた。

充分洗浄した再生型 (OH 型) の SBAER を, あらかじめ窒素ガスを吹き込んだ精製純水中で 100 d, 50°C で浸漬した。溶出してきた溶出物量は 1 L 湿潤樹脂の乾燥樹脂当たり 1.4×10^{-1} から 3.0 mgC/h で, その主成分は官能基の分解物であるトリメチルアミンであった。溶出物はゲル透過クロマトグラフ分析の結果, 高分子量成分としては, ポリスチレンスルホン酸塩換算分子量で 500 以上 1 万以下の範囲にあり, 分子量 2,200, 4,000 及び 5,900 の 3 成分が共通して含まれていることがわかった。逆相クロマトグラフ分析で, 低分子量成分中に含まれる芳香族の溶出物の構造を推定した。

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