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# Separation of perfluoroalkylsulfonic acids and perfluoroalkylsulfonic acids by ion-exclusion chromatography

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## Abstract

Ion-exclusion chromatography has been successfully applied to the separation of a number of perfluoroalkylsulfonic acids and perfluoroalkylsulfonic acids. The separation of various perfluoroalkylsulfonic and perfluoroalkylsulfonic acids, with different alkyl groups, was investigated on a polymethacrylate-based, weakly acidic, cation-exchange resin (TSK gel OApak-A) in the H<sup>+</sup>-form and using conductimetric detection. When water was used as the eluent, these perfluoroalkylsulfonic and perfluoroalkylsulfonic acids could not be resolved. When an aqueous solution of benzoic acid and *o*-phthalic acid was used, the separation of each of these acids occurred. In order to improve their separation, the effect of the addition of methanol and 2,2,2-trifluoroethanol, as organic modifiers, was also investigated. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Mobile-phase composition; Perfluoroalkylsulfonic acids; Perfluoroalkylsulfonic acids; Organic acids; Organofluorine compounds; Organosulfur compounds

## 1. Introduction

Perfluoroalkylsulfonic acids are widely used as starting materials, as are perfluorocarboxylic acids, for making versatile fluoropolymers, fluorosurfactants, textile finishers and so on [1–3]. In contrast, perfluoroalkylsulfonic acids [4] have recently been used as a source of fluoroalkyl radicals in an aqueous emulsion–polymerization reaction [5], although they have not been used widely in industrial applications, compared to perfluoroalkylcarboxylic acids and perfluoroalkylsulfonic acids. As they have a four-valent sulfur atom, perfluoroalkylsulfonic acids can be transformed into the corresponding perfluorosulfonic acids, which have a hexavalent sulfur, by an oxida-

tion reaction. Both perfluoroalkylsulfonic and perfluoroalkylsulfonic acids have a unique character that is associated primarily with the presence of a fluorine atom in the alkyl group, compared with the more usual alkylsulfonic and alkylsulfonic acids. For example, due to the inductive effect of the fluorine atom in the alkyl group of perfluoroalkylsulfonic and perfluoroalkylsulfonic acids, these two acids show strong acidity, similar to that of polyfluoroalkylcarboxylic acids [2,3]. In addition, the perfluoroalkyl group has a lower surface energy than those of usual hydrocarbonous alkyl group. The characteristics, such as strong acidity, low surface energy, and strong hydrophobic character, of perfluoroalkyl groups, which are the same as those of perfluorocarboxylic acids, makes it difficult to analyze them by means of conventional liquid chromatography [6–8].

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To the best of our knowledge, the analysis of perfluoroalkylsulfonic acids and perfluoroalkylsulfonic acids by ion-exclusion chromatography has not been reported [9–12].

We have shown in a previous paper that polyfluorocarboxylic acids could be separated by means of ion-exclusion chromatography with conductimetric detection [13]. In view of the same strong acidity among perfluorocarboxylic acids, perfluorosulfonic acids and perfluorosulfonic acids, it seemed of interest to compare the behavior of ion-exclusion chromatographic separation between perfluorocarboxylic acids, and perfluorosulfonic and perfluorosulfonic acids. This study was undertaken in order to examine the application and limitations of the analysis of various types of perfluoroalkylsulfonic acids and perfluoroalkylsulfonic acids by ion-exclusion chromatography.

## 2. Experimental

### 2.1. Apparatus

A Shimadzu ion chromatograph, model LC-10 (Kyoto, Japan) was used, which consisted of a system controller SCL-10A (Kyoto, Japan), a conductivity detector CDD-6A (Kyoto, Japan), a model LC-10AD (Kyoto, Japan) eluent delivery pump with a Rheodyne sample injector (20  $\mu$ l), a column oven CTO-10A (Kyoto, Japan) with a constant temperature controller at 40°C, a model Shodex degasser (Tokyo, Japan), and a Chromatopac C-R6A (Kyoto, Japan) for data collection and processing.

### 2.2. Column

Two columns connected in series were used. A Tosoh stainless-steel column containing TSKgel OApak-P (6.0 $\times$ 4 cm; a strongly acidic cation-exchange resin) was used as the pre-column, to remove cationic species. As the separation column, a Tosoh stainless-steel column packed with TSKgel OApak-A (30 cm $\times$ 7.8 mm) (polymethacrylate-based weakly acidic cation-exchange resin in the H<sup>+</sup> form with a particle size of 5  $\mu$ m) was used. The column was equilibrated thoroughly with the eluent before the chromatographic run.

### 2.3. Reagents and solutions

#### 2.3.1. Preparation of reagents

Standard solutions of five alkali metal salts of perfluoroalkylsulfonic acids and five alkali metal salts of perfluoroalkylsulfonic acids were prepared for this experiment. Perfluoroalkylsulfonic acids and their alkali metal salts were not available commercially. Therefore, all alkali metal salts of perfluoroalkylsulfonic acids used in this work, such as sodium trifluoromethylsulfinate (**1a**), sodium pentafluoroethylsulfinate (**1b**), potassium perfluoropropylsulfinate (**1c**), potassium perfluorobutylsulfinate (**1d**) and potassium perfluorohexylsulfinate (**1e**), were made according to the method reported in the literature [14,15]. Although several methods have been reported for the preparation of perfluoroalkylsulfonic acids, it was found that the purity of the perfluoroalkylsulfonic acids synthesized varied depending on the preparative method used. For example, potassium salts of **1a–1e** were prepared by the reaction of the corresponding perfluoroalkyliodides with potassium sulfite [14]. However, of them, **1a** and **1b** contained considerable amounts of impurities, which could not be removed by conventional purification procedures. Therefore, sodium salts of **1a** and **1b**, instead of made from potassium salts, were made via an alternative route, i.e., reaction of the corresponding perfluoroalkylsulfonyl fluoride [R<sub>F</sub>SO<sub>2</sub>F: R<sub>F</sub>=CF<sub>3</sub>, C<sub>2</sub>F<sub>5</sub>] with sodium azide in methanol [15]. Perfluoroalkylsulfonyl fluorides were prepared by the electrochemical fluorination of the corresponding alkylsulfonyl chlorides [4], and purified by low-temperature distillation. Three reagents such as sodium trifluoromethylsulfonate (**2a**) (Wako, Osaka, Japan), potassium perfluorobutylsulfonate (**2d**) (Tohkem, Tokyo, Japan) and barium pentafluorophenylsulfonate (**2e**) (Wako) were used as received. Two alkali metal salts of perfluoroalkylsulfonates including sodium pentafluoroethylsulfonate (**2b**) and sodium perfluoropropylsulfonate (**2c**) were made by the reaction of the corresponding perfluoroalkylsulfonyl fluorides (R<sub>F</sub>SO<sub>2</sub>F: R<sub>F</sub>=C<sub>2</sub>F<sub>5</sub>, C<sub>3</sub>F<sub>7</sub>) with (CH<sub>3</sub>)<sub>3</sub>SiONa (Aldrich, USA), which were then purified by recrystallization with a mixture of ethanol and CHCl<sub>3</sub>. The concentration of each of the standard solutions was adjusted to a concentration of 20 ppm, and two

mixtures of sample solutions (Groups 1 and 2) were made. Group 1 consisted of a mixture of five solutions of perfluoroalkylsulfonic acids, having a perfluoroalkyl chain containing one–six carbons. Group 2 consisted of a mixture of five solutions of perfluoroalkylsulfonic acids, with various perfluoroalkyl groups. While Group 2 was stable against hydrolysis, Group 1 showed an indication of gradual decomposition into perfluoroacids, fluoride ion and the corresponding perfluorosulfonic acids. Therefore, the sample solutions of Group 1 were made freshly and stored in a refrigerator before analysis. As an indicator, a solution containing 2 ppm  $\text{H}_2\text{SO}_4$  was added to them. Thus, two sample solutions of a mixture of sulfonic acids and sulfonic acids were prepared:

Group 1:  $\text{CF}_3\text{S}(\text{O})\text{ONa}$  (**1a**),  $\text{C}_2\text{F}_5\text{S}(\text{O})\text{ONa}$  (**1b**),  $n\text{-C}_3\text{F}_7\text{S}(\text{O})\text{OK}$  (**1c**),  $n\text{-C}_4\text{F}_9\text{S}(\text{O})\text{OK}$  (**1d**),  $n\text{-C}_6\text{F}_{13}\text{S}(\text{O})\text{OK}$  (**1e**)

Group 2:  $\text{CF}_3\text{S}(\text{O})_2\text{ONa}$  (**2a**),  $\text{C}_2\text{F}_5\text{S}(\text{O})_2\text{ONa}$  (**2b**),  $n\text{-C}_3\text{F}_7\text{S}(\text{O})_2\text{ONa}$  (**2c**),  $n\text{-C}_4\text{F}_9\text{S}(\text{O})_2\text{OK}$  (**2d**),  $[\text{C}_6\text{F}_5\text{S}(\text{O})_2\text{O}]_2\text{Ba}$  (**2e**)

### 2.3.2. Eluents

The eluents, consisting of benzoic acid and *o*-phthalic acid, were prepared by dissolving the acids and organic solvents in distilled, deionized water and filtering them through a 0.45- $\mu\text{m}$  filter.

## 3. Results and discussion

### 3.1. Ion-exclusion chromatographic separation of perfluoroalkylsulfonic acids and perfluorosulfonic acids

In ion chromatography, water or an aqueous solution of sulfuric acid is generally used as the eluent [6,8]. When water was used as an eluent in the present ion-exclusion chromatography study, peaks of perfluoroalkylsulfonic acids and of perfluoroalkylsulfonic acids could not be resolved.

We have shown in a previous paper that polyfluorocarboxylic acids could be successfully resolved by using aqueous solutions of weak organic acids (tartaric acids, benzoic acid, *o*-phthalic acid, 1,3,5-benzenetricarboxylic acid and 1,2,4,5-benzenetetracarboxylic acid) in place of water as the eluent

[13]. It is thought that the hydrophobic character of the matrix of the column, which is provided by the adsorption of weak organic acids from the eluent in an equilibrium state, plays an important role in the separation of polyfluorocarboxylic acids [16,17]. Among these organic acids, the use of aqueous solutions such as benzoic acid, *o*-phthalic acid and tartaric acid afforded rather good results for the separation of various polyfluorocarboxylic acids, when points such as (1) the degree of separation of the peaks corresponding to each of the carboxylic acids, (2) the interruption by the appearance of the system peak (the difference of retention volumes ( $V_R$ ) between the system peak and the targeted polyfluorocarboxylic acids), and (3) the stability of the baseline [13]. Therefore, in the present investigation, two aqueous solutions, benzoic acid and *o*-phthalic acid, were selected as eluents.

When benzoic acid (concentration, 2–10 mM) was used as the eluent (Fig. 1; eluent, 6 mM benzoic acid), trifluoromethylsulfonic acid (**1a**), pentafluoroethylsulfonic acid (**1b**), perfluoropropylsulfonic acid (**1c**), perfluorobutylsulfonic acid (**1d**) and perfluoroheptylsulfonic acid (**1e**) eluted successfully in order of increasing carbon number of the alkylsulfonic acids. Two peaks appeared before the peak of **1a**, although these two peaks did not interfere with the peaks of perfluoroalkylsulfonic acids. One of the two peaks was assigned to  $\text{SO}_3^{2-}$ , based on comparison with the retention volumes of authentic sample on the chromatogram.

Similarly, the ion-exclusion chromatographic separation of perfluoroalkylsulfonic acids (**1a–1d**) was investigated using an aqueous solution of *o*-phthalic acid (concentration, 2–10 mM) as an eluent and the same order of elution as found with benzoic acid eluent was observed for **1a**, **1b**, **1c** and **1d**. However, in a manner different from that with benzoic acid as eluent, the peak of **1e**, which has a stronger hydrophobic character due to its having the longest perfluoroalkyl group among the Group 1 solution, eluted with a very large retention time (99.6 min) under comparable analytical conditions (Fig. 2; eluent, 6 mM *o*-phthalic acid). Furthermore, it was found that two peaks ( $\text{H}_2\text{SO}_4$  and  $\text{SO}_3^-$ ) coeluted before **1a**.

When benzoic acid (concentration: 2 mM) was used as an eluent, trifluoromethylsulfonic acid (**2a**),

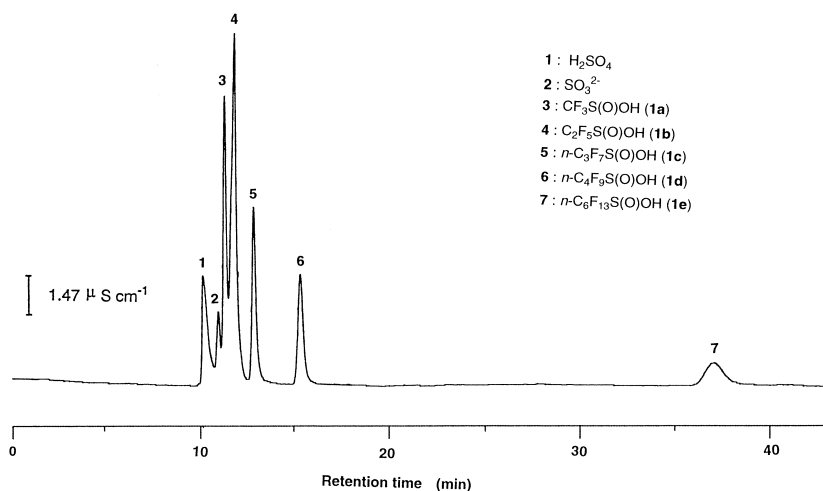


Fig. 1. Ion-exclusion chromatogram of perfluoroalkylsulfonic acids (Group 1) by elution with 6 mM benzoic acid. Column, TSKgel OApak-A (polymethacrylate-based, weakly acidic, cation-exchange resin in the  $H^+$  form) (30 cm $\times$ 7.8 mm I.D.); Column temperature, 40°C; flow-rate, 0.6 ml/min; sample concentration, 20 ppm perfluoroalkylsulfonic acids; conductimetric detection sensitivity, 1  $\mu$ S/cm = 10 mV. Peaks: 1,  $H_2SO_4$ ; 2,  $SO_3^{2-}$ ; 3, **1a**; 4, **1b**; 5, **1c**; 6, **1d** and 7, **1e**.

pentafluoroethylsulfonic acid (**2b**), perfluoropropylsulfonic acid (**2c**) and perfluorobutylsulfonic acid (**2d**) could be separated in order of increasing carbon number of the perfluoroalkylsulfonic acids, however, pentafluorophenylsulfonic acid (**2e**) co-eluted with pentafluoroethylsulfonic acid (**2b**) under the conditions used. However, these two peaks were successfully separated (**2b** < **2e**) by using a higher concentration of benzoic acid (Fig. 3; eluent, 6 mM

benzoic acid). Thus, the order of elution of perfluorosulfonic acids was **2a** < **2b** < **2c** < **2d**. It was observed that pentafluorophenylsulfonic acid (**2e**) eluted faster than **2c** and **2d** among the acids of Group 2, which may be ascribed to the size-exclusion effect. When *o*-phthalic acid was used as an eluent, the same order of elution of sulfonic acids was observed as that obtained with benzoic acid as

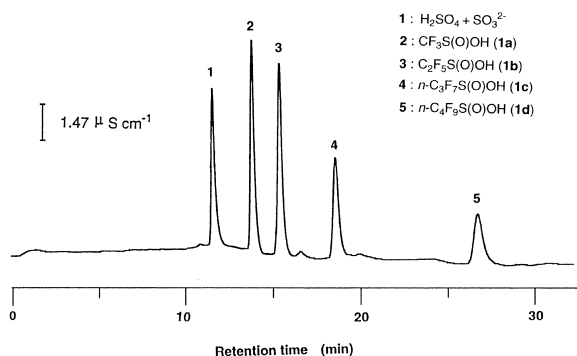


Fig. 2. Ion-exclusion chromatogram of perfluoroalkylsulfonic acids (Group 1) by elution with 6 mM *o*-phthalic acid. Other chromatographic conditions are the same as in Fig. 1. Peaks: 1,  $H_2SO_4 + SO_3^{2-}$ ; 2, **1a**; 3, **1b**; 4, **1c** and 5, **1d**. The peak for **1e** appeared at a retention time of 99.5 min.

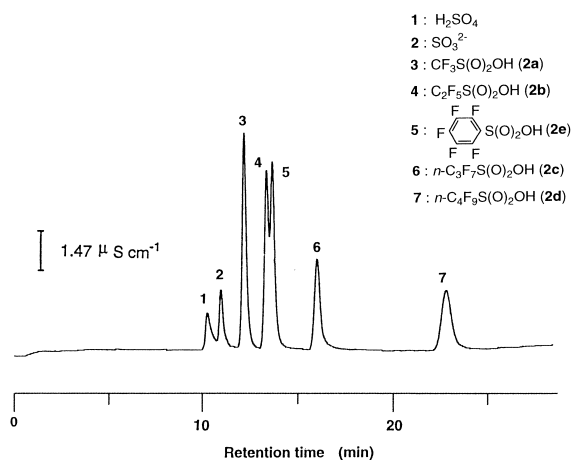


Fig. 3. Ion-exclusion chromatogram of perfluoroalkylsulfonic acids (Group 2) by elution with 6 mM benzoic acid. Other chromatographic conditions were the same as in Fig. 1. Peaks: 1,  $H_2SO_4$ ; 2,  $SO_3^{2-}$ ; 3, **2a**; 4, **2b**; 5, **2e**; 6, **2c** and 7, **2d**.

eluent, but the retention volumes were much larger than those obtained with benzoic acid.

### 3.2. Distribution coefficient of perfluoroalkylsulfonic acids and perfluoroalkylsulfonic acids

The retention volumes of perfluoroalkylsulfonic acids and perfluoroalkylsulfonic acids were measured with various *o*-phthalic acid and benzoic acid eluents. Those calculated from the data with 6 mM benzoic acid as eluent and with 6 mM *o*-phthalic acid as eluent are summarized in Table 1. The distribution coefficients were calculated by assuming  $K_d = 1.00$  for methanol [18].

Perfluoroalkylsulfonic acids are among the strongest acids known. For example, measurements of the conductivity of trifluoromethylsulfonic acid in acetic acid have shown that it is one of the strongest protic acids and is comparable to fluorosulfonic and perchloric acids [19,20]. It is considered that analogues of polyfluoroalkylsulfonic acids have dissociation constants of almost the same order as that of trifluoromethylsulfonic acid. It is known that the distribution coefficients of carboxylic acids increase with increasing  $pK_a$  [2,3,18]. Therefore, for the ion-exclusion chromatographic separation of most of the perfluoroalkylsulfonic acids and perfluoroalkylsulfonic acids, it was considered that an ion-exclusion effect was the predominant factor both for these

perfluoroalkylsulfonic acids and for perfluoroalkylsulfonic acids with a short alkyl chain length [10,13,16]. As can be seen in Table 1, the order of  $K_d$  values for the perfluoroalkylsulfonic acids studied was  $1a < 1b < 1c < 1d < 1e$ , which is in accordance with an increase in the carbon number of the perfluoroalkyl group. The  $V_R$  of **1e** was found to be very large when *o*-phthalic acid was used as the eluent. As perfluorohexylsulfonic acid (**1e**) has the longest perfluoroalkyl groups, with strong hydrophobic properties, among Group 1 solutions, a hydrophobic absorption of **1e** towards column resin seems to be the major factor for its high  $V_R$  value. Similarly, it was observed that the order of  $K_d$  values for perfluoroalkylsulfonic acids, with the exception of **2e**, was  $2a < 2b < 2c < 2d$ . The  $K_d$  value for **2e** was between those of **2b** and **2c**. By considering the total six carbon number of the pentafluorophenyl group of **2e** compared with the linear perfluoropropyl group of **2c**, it was considered that the size-exclusion effect was the predominant factor for **2e**.

### 3.3. Effect of the concentration of benzoic acid and *o*-phthalic acid on the retention volumes of perfluoroalkylsulfonic acids and perfluoroalkylsulfonic acids

In order to examine the effect of the concentration of eluents (benzoic acid and *o*-phthalic acid) on the

Table 1

Retention volumes ( $V_R$ ) and distribution coefficients ( $K_d$ ) of acids (perfluoroalkylsulfonic acids and perfluoroalkylsulfonic acids) with 6 mM benzoic acid and 6 mM *o*-phthalic acid as eluents<sup>a</sup>

Acid	Benzoic acid eluent <sup>b</sup>		<i>o</i> -Phthalic acid eluent <sup>b</sup>	
	$V_R$ (ml)	$K_d$	$V_R$ (ml)	$K_d$
Void (sulfuric acid)	6.1	0	6.8	0
CH <sub>3</sub> OH	12.0	1	12.0	1
CF <sub>3</sub> S(O)OH ( <b>1a</b> )	6.7	0.10	8.2	0.27
C <sub>2</sub> F <sub>5</sub> S(O)OH ( <b>1b</b> )	7.0	0.17	9.1	0.44
<i>n</i> -C <sub>3</sub> F <sub>7</sub> S(O)OH ( <b>1c</b> )	7.6	0.25	11.0	0.81
<i>n</i> -C <sub>4</sub> F <sub>9</sub> S(O)OH ( <b>1d</b> )	9.1	0.51	15.8	1.73
<i>n</i> -C <sub>6</sub> F <sub>13</sub> S(O)OH ( <b>1e</b> )	22.0	2.70	59.7	10.17
CF <sub>3</sub> S(O) <sub>2</sub> OH ( <b>2a</b> )	7.2	0.19	9.7	0.56
C <sub>2</sub> F <sub>5</sub> S(O) <sub>2</sub> OH ( <b>2b</b> )	7.9	0.31	11.9	0.98
<i>n</i> -C <sub>3</sub> F <sub>7</sub> S(O) <sub>2</sub> OH ( <b>2c</b> )	9.5	0.58	17.1	1.98
<i>n</i> -C <sub>4</sub> F <sub>9</sub> S(O) <sub>2</sub> OH ( <b>2d</b> )	13.5	1.25	30.7	4.60
C <sub>6</sub> F <sub>5</sub> S(O) <sub>2</sub> OH ( <b>2e</b> )	8.1	0.34	12.2	1.04

<sup>a</sup>  $K_d = (V_R - V_0) / V_i$ .  $V_i$  is the volume of eluent inside the resin beads.

<sup>b</sup> 6 mM.

retention volume of perfluoroalkylsulfonic and perfluoroalkylsulfonic acids, the ion-exclusion chromatographic separation of Group 1 and Group 2 solutions was investigated at several concentrations of each of the eluents in the range of 2–10 mM. The relationship between the concentration of eluents (benzoic acid and *o*-phthalic acid) and the  $V_R$  values of perfluoroalkylsulfonic and perfluoroalkylsulfonic acids are summarized in Table 2. It was found that the  $V_R$  values of both perfluorosulfonic and perfluorosulfonic acids increased with an increase in the concentration of the eluent (benzoic acid and *o*-phthalic acid).

No correlation was observed between the concentration of eluent and the detection sensitivity. This was probably because these perfluoroalkylsulfonic acids and perfluoroalkylsulfonic acids are completely ionized over the pH range of the eluents employed (pH 3.04–3.77 for benzoic acid and pH 2.36–3.39 for *o*-phthalic acid).

### 3.4. Effect of organic modifier

It is known that the addition of organic modifier can reduce the adsorption effects of hydrophobic carboxylic acids to the cation-exchange resin and thus decrease  $V_R$  values [7,6,17]. In order to accelerate the elution of hydrophobic perfluoroalkylsulfonic

acids and perfluoroalkylsulfonic acids, the effect of the addition of organic modifier was examined using *o*-phthalic acid as the eluent. The effects of the addition of organic modifier (methanol and 2,2,2-trifluoroethanol) to 6 mM *o*-phthalic acid are shown in Table 3. It was found that the peak of perfluorohexylsulfonic acid (**1e**), which appeared at a very high retention time with *o*-phthalic acid as the eluent, could be detected with a shortened  $V_R$  by the addition of either methanol or 2,2,2-trifluoroethanol. For example, the  $V_R$  of **1e** could be reduced by more than half, from 59.7 to 24.1 ml, by the addition of 20% methanol. Furthermore, different retention volumes were observed between these two alcohols. Due to the electron-withdrawing effect of the fluorine atom, 2,2,2-trifluoroethanol has a more acidic character than methanol [2]. However, such an apparent difference in retention volumes between 2,2,2-trifluoroethanol and methanol will be attributed mainly to the hydrophobic interaction towards the resin network, as the former compound has greater hydrophobic nature due to the presence of  $\text{CF}_3$ -group than the latter one.

### 3.5. Calibration graphs of perfluoroalkylsulfonic acids and perfluoroalkylsulfonic acids

Under the chromatographic conditions with 6 mM

Table 2  
Effect of concentration of eluents on retention volumes ( $V_R$ ) of acids (perfluoroalkylsulfonic acids and perfluoroalkylsulfonic acids)

Sample	Eluent: benzoic acid				Eluent: <i>o</i> -phthalic acid				
	2 mM	4 mM	6 mM	8 mM	2 mM	4 mM	6 mM	8 mM	10 mM
H <sub>2</sub> SO <sub>4</sub> ( $V_R$ )	6.0	6.1	6.1	6.2	6.2	6.6	6.8	6.9	7.1
Group 1									
<b>1a</b>	6.4	6.6	6.7	6.9	7.3	7.8	8.2	8.4	8.5
<b>1b</b>	6.6	6.8	7.0	7.2	7.9	8.6	9.1	9.4	9.6
<b>1c</b>	6.9	7.4	7.6	7.8	9.1	10.9	11.0	11.4	11.8
<b>1d</b>	7.9	8.7	9.1	9.5	12.1	14.5	15.9	16.6	17.2
<b>1e</b>	16.8	20.0	22.1	23.4	41.0	53.4	59.7	<sup>a</sup>	<sup>a</sup>
Group 2									
<b>2a</b>	6.7	7.0	7.2	7.4	8.2	9.2	9.7	10.1	10.3
<b>2b</b>	7.2	7.7	7.9	8.1	9.6	11.1	11.9	12.4	12.8
<b>2c</b>	8.2	9.0	9.5	10.1	13.0	15.7	17.2	18.0	18.6
<b>2d</b>	11.0	12.6	13.5	14.1	22.0	27.8	30.9	32.4	33.5
<b>2e</b>	7.2	7.7	8.1	8.3	9.8	11.4	12.3	12.8	13.2
BG (mS/cm)	176	265	335	398	616	957	1226	1443	1635

<sup>a</sup> —, very large  $V_R$ .

Table 3

Effect of the concentration of modifier in the eluent on the retention volumes ( $V_R$ ) of acids (perfluoroalkylsulfonic acids and perfluoroalkylsulfonic acids)

Sample	Eluent: 6 mM methanol				Eluent: 6 mM 2,2,2-trifluoroethanol				
	5%	10%	15%	20%	1%	2%	5%	10%	15%
Alcohol ( $V_R$ )	11.6	11.7	11.7	11.6	17.1	16.8	16.3	15.5	14.4
Group 1									
<b>1a</b>	8.1	8.0	8.0	7.9	8.1	8.1	7.9	7.7	7.7
<b>1b</b>	9.0	8.8	8.7	8.6	9.0	8.9	8.7	8.4	8.4
<b>1c</b>	10.6	10.2	9.9	9.6	10.7	10.6	10.2	9.7	9.7
<b>1d</b>	14.6	13.5	12.6	11.6 <sup>a</sup>	15.1	14.7	13.9	12.8	12.8
<b>1e</b>	47.4	37.5	30.4	24.1	53.6	50.7	44.7	35.6	35.6
Group 2									
<b>2a</b>	9.5	9.3	9.1	8.9	9.4	9.3	8.8	8.3	7.9
<b>2b</b>	11.3	11.1	10.6	10.2	11.3	10.9	10.1	9.2	8.6
<b>2c</b>	15.6	14.4	13.4	12.4	15.7	14.9	13.2	11.3	10.0
<b>2d</b>	26.1	22.5	19.7	17.2	27.0	24.9	20.6	15.5 <sup>b</sup>	13.1
<b>2e</b>	11.6	11.1	10.6	10.2	11.8	10.9	10.6	9.6	9.0
BG ( $\mu\text{S}/\text{cm}$ )	1050	899	769	654	1175	1141	1030	867	725

<sup>a</sup> This peak coincided with the peak of methanol.

<sup>b</sup> This peak coincided with the peak of 2,2,2-trifluoroethanol.

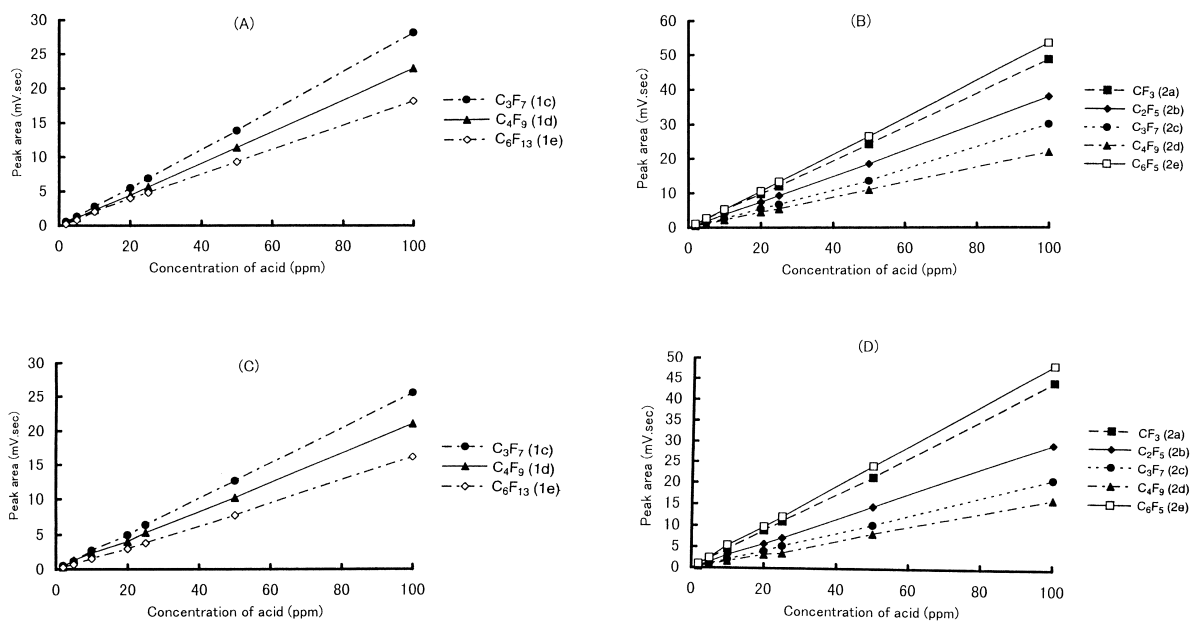


Fig. 4. Calibration curve of a mixture of perfluoroalkylsulfonic acids (graphs A and C) and perfluoroalkylsulfonic acids (graphs B and D) in the range of 2–100 ppm by elution with 6 mM benzoic acid (graphs A and B) and 6 mM *o*-phthalic acid (graphs C and D). Other chromatographic conditions are as in Fig. 1.

benzoic acid and 6 mM *o*-phthalic acid as eluent, calibration curves were obtained by plotting the peak area of perfluoroalkylsulfonic acids (graphs A and C) and perfluoroalkylsulfonic acids (graphs B and D) vs. the concentration of eluent (Fig. 4). Because of the presence of impurities in trifluorosulfonic acid (**1a**) and pentafluoroethylsulfonic acid (**1b**) and because they are unstable in aqueous solution, graphs A and C of Fig. 4 were made without the data for **1a** and **1b**. Peak areas (mV s) were obtained by varying the concentration from 2 to 100 ppm for each sample solution of acid. Thus, a linear relationship was obtained for these acids of Groups 1 and 2 in the concentration range of 2 to 100 ppm.

#### 4. Conclusion

The ion-exclusion chromatography of perfluoroalkylsulfonic acids and perfluoroalkylsulfonic acids was investigated using a column of TSKgel OApak-A, a weakly acidic, cation-exchange resin. Good resolution, both of sulfonic acids and sulfonic acids, was accomplished by elution with organic acid (benzoic acid and *o*-phthalic acid) solutions. This investigation has provided a new analytical method for the determination of perfluoroalkylsulfonic acids and perfluoroalkylsulfonic acids by ion-exclusion chromatography.

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