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Separation of Aromatic Carboxylic Acids Using Quaternary Ammonium Salts on Reversed-Phase HPLC. 2. Application for the Analysis of Loy Yang Coal Oxidation Products

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Abstract: In order to develop separation processes and analytical methods for aromatic carboxylic acids for the coal oxidation products, the separation behavior of aromatic carboxylic acids on a reversed-phase HPLC using eluent containing quaternary ammonium salt was optimized using the solvent gradient method. This method was applied for the analysis of Loy Yang coal oxidation products. It was confirmed that the analytical data using this method were consistent with those determined using gas chromatography.

Keywords: High performance liquid chromatography, aromatic carboxylic acid, coal oxidation products, alkaline solution at high temperature, quaternary ammonium salt, ion-pair solvent extraction

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INTRODUCTION

Oxidation of coal in aqueous solutions at high temperatures is a useful technique for the utilization of different rank of coal resources (1–5). Oxalic acid and acetic acid are possible to obtain from the coal oxidation in acidic and alkaline solutions (6–11) as well as a pilot operation of the coal oxidation in alkaline solution and a continuous removal technique of carbon dioxide for the coal oxidation in alkaline solution at high temperatures were developed (12–14). Additionally, several applications have been attempted by our group (15, 16).

On the other hand, a large extent of water-soluble aromatic polycarboxylic acids can be obtained in the coal oxidation products, where the total yields of aromatic carboxylic acids sometimes reach to 50 wt% of the oxidation products (16). However, useful applications of the production of aromatic carboxylic acids from coal have not been adequately established. Practical industrial applications carried out are dependent on the relative costs of petroleum and coal, and the demand of aromatic polycarboxylic acids (17–19). Additionally, the efficient and practical analytical methods of these aromatic carboxylic acids have not been developed since the coal oxidation products involve a fairly complicated mixture of carboxylic acid isomers since there are few systematic investigations on the analysis of aromatic carboxylic acids (20–24). Normally, these products have been analyzed using gas chromatography (GC). However, the derivation of methyl esters from aromatic carboxylic acids is necessary. In our previous studies, solvent extraction behavior (25) and separation behavior on HPLC for aromatic polycarboxylic acids was investigated.

In this study, the separation method of benzene polycarboxylic acids using the reversed-phase HPLC in the presence of quaternary ammonium has been optimized without the derivation to methyl esters (25). Moreover, the separation of coal oxidation products was attempted and the results were compared with data obtained by GC-MS analysis.

EXPERIMENTAL

Materials and Apparatus

All reagents used were of extra pure grade. Separation behavior of aromatic carboxylic acids was analyzed using a HPLC system consisting of UVIDEC-100V, TRIROTAR-S, and M6000 pump (JASCO, Japan) on a reversed-phase column (Merck LichroCART 125-4 RP-18) at 0.5 mL min^{-1} at 30°C. Samples were detected at 254 nm. A 2360 ISCO gradient programmer was used for the solvent gradient control. Abbreviations are following; tetrabuthylammonium bromide: TBABr, trimethyl-n-octylammonium bromide: TMOABr, trimethyl-n-hexylammonium bromide: TMHABr, benzoic acid: 1BE, 1,2-benzenedicarboxylic acid: 12BE, 1,3-benzenedicarboxylic acid: 13BE, 1,4-benzenedicarboxylic acid: 14BE, 1,3,5-benzenetricarboxylic acid: 135BE, 1,2,4-benzenetricarboxylic acid: 124BE, 1,2,3-benzenetricarboxylic acid: 123BE, 1,2,4,5-benzenetetracarboxylic acid: 1245BE, 1,2,3,4,5-benzenepentacarboxylic acid: 12345BE, 1,2,3,4,5,6-benzenehexacarboxylic acid: 123456BE.

Coal Oxidation and Analysis by Gas Chromatography

A mixture involving 2 g of coal, 25 g distilled water, and a few grams of NaOH of Na_2CO_3 was placed in a 70 mL stainless steel autoclave. After the air was replaced with oxygen, the mixture was heated for 2 h and cooled immediately. The mixture was dissolved in 100 mL distilled water. Water-soluble aromatic acids and water-insoluble acids were separated from the oxidation products by previous method. The water-soluble aromatic acids were extracted into ethylmethylketone (MEK) and methyl ester of the aromatic acids were derived using diazomethane for the MEK extract. The MEK extract was directly analyzed by HPLC and the methyl esters were analyzed by gas chromatography (GC). Details of elemental analysis and gas chromatography were followed a previous method (5, 15, 16). A Hewlett Packard 5890/8970 GC/MSD system with a 25 m column (0.22 mm inner diameter) coated with 5% phenylmethylsilicon phase was used for analysis of coal oxidation products.

RESULTS AND DISCUSSION

HPLC Conditions for the Separation of Aromatic Carboxylic Acids

According to the separation behavior of 10 kinds of benzenecarboxylic acids, the separation was attempted using solvents containing TBABr, TMOABr, or TMHABr in methanol-water system. The separation of isomers possessing the same number of carboxylic groups, such as 12BE, 13BE, and 14BE was difficult unless using solvent containing TMOABr. The optimum separation was achieved using a solvent containing 3.5 mmol kg^{-1} TMOABr and 35% methanol. In addition, to facilitate to elute the analytes, solvent gradient was attempted. Samples were analyzed using a solvent containing 3.5×10^{-3} mol kg^{-1} TMOABr at pH 7.6 (sodium acetate) using a methanol gradient of 31.5% methanol at 0–15 min, linearly increase at 15–35 min, 40.2% at 35–75 min. It was found that small modification of the solvent gradient program was necessary if different reversed-phase columns were obtained to use from other manufactures.

The chromatograms of authentic samples using isocratic separation condition are shown in Fig. 1. The detection limits were calculated on the basis of signal to noise ratio = 3 (Table 1). The retention times of benzene tetra-, penta-, and hexacarboxylic acids were fairly sensitive to the purity of

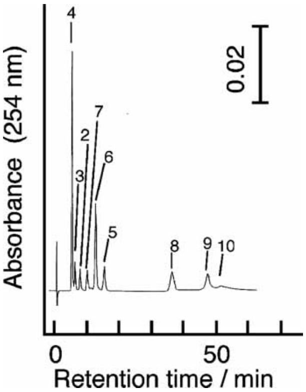

Figure 1. HPLC chromatogram obtained using isocratic separation condition for a standard sample mixture. Flow rate: 0.5 mL min^{-1}, 254 nm, 30°C, pH = 7.6, TMOABr: 3.5×10^{-3} mol kg^{-1}.

distilled water and tailing was observed for benzenehexacarboxylic acid. These were resolved using gradient control of methanol content.

Analysis of the Oxidation Products of Loy Yang Coal

The nature of Loy Yang coal used in this study is summarized in Table 2 and the coal oxidation products were summarized in Table 3. The analyses are

Table 1. Detection limits of benzenepolycarobxylic acids at 254 nm

Bezenepolycarboxylic acids	Detection limits/10^{-7} M
1,2-BE	9.1
1,3-BE	6.1
1,4-BE	0.74
1,2,3-BE	7.4
1,2,4-BE	2.1
1,3,5-BE	7.0
1,2,4,5-BE	8.3
1,2,3,4,5-BE	12.0
1,2,3,4,5,6-BE	20.0

Standard deviation of base line noise corresponds to 1.5×10^{-5} absorbance unit. The detection limits were calculated on the basis of S/N = 3.

Abbreviations, 12BE: 1,2-benzenedicarboxylic acid, 13BE: 1,3-benzenedicarboxylic acid, 14BE: 1,4-benzenedicarboxylic acid, 135BE: 1,3,5-benzenetricarboxylic acid, 124BE: 1,2,4-benzenetricarboxylic acid, 123BE: 1,2,3-benzenetricarboxylic acid, 1245BE: 1,2,4,5-benzenetetracarboxylic acid, 12345BE: 1,2,3,4,5-benzenepentacarboxylic acid, 123456BE: 1,2,3,4,5,6-benzenehexacarboxylic acid.

Table 2. Composition of Loy Yang coal

Composition (wt%)						
C	H	N	S	O	Ash (wt%)	Moisture (wt%)
68.3	4.9	0.61	0.75	25.94	1.0	67.5

consistent with a previous study (15). First, the gas chromatography analysis was carried out for the oxidation products. The gas chromatograms are shown in Fig. 2 and the relative extents of benzenepolycarboxylic acids are summarized in Table 4. It was confirmed that a large amount of benzene tri-, tetra-, and pentacarboxylic acids were observed and a small amount of benzenehexacarboxylic acid, bezoic acid, and phthalic acid isomers were identified. Greater extents of benzenepolycarboxylic acids were produced under higher concentration of NaOH or using Na_2CO_3. A very small amount of methylbenzenecarboxylic acid was observed. The extents and the type of aromatic acids found in the products are basically consistent with those of Yallourn coal (15).

On the other hand, the MEK extracts without derivation to methyl esters were also analyzed HPLC and the results are summarized in Table 5. It was found that the retention times of 1245BE, 12345BE, and 123456BE were fairly affected. This is probably due to the fact that the coal oxidation products contain complicated matrix using after the MEK extracts, which would affected the separation of the analytes. Thus, 1245BE, 12345BE, and 123456BE were identified by coinjection of the authentic 1245BE, 12345BE, and 123456BE samples.

Table 3. Reaction conditions and extent of the oxidation products of Loy Yang coal

Run	1	2	3
Conditions			
Coal (g)	5	5	5
Water (g)	25	25	25
NaOH (g)	5	0	10
Na_2CO_3	0	6.6	0
PO_2 (kg cm^{-2})	30	30	50
T/K	523	523	523
Time/h	2	2	2
Products (wt%)			
MEK extract	78.8	46.2	58.1
Water insoluble	13.6	17.0	0.85
Oxalic acid	42.8	5.9	33.3
Residue	0.69	12.4	0.0

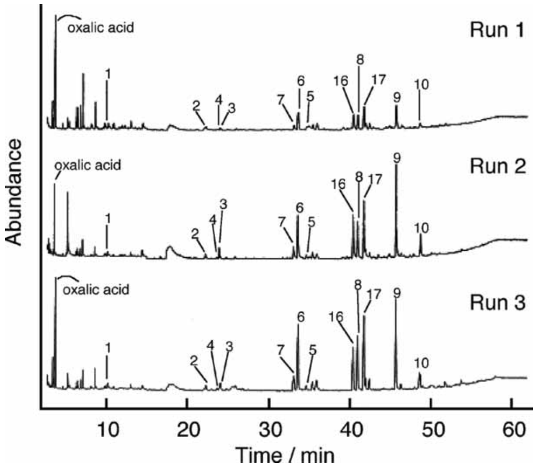

Figure 2. GC chromatograms obtained for the MEK extract of coal oxidation products. Numbers for aromatic carboxylic acids are shown in Table 1.

The results by HPLC (Figure 3) were compared with those determined using GC. In spite of the fact that there are so many unknown products found in HPLC other than the standard polycarboxylic acids, the extent of benzenepolycarboxylic acids fairly coincided with GC data. Run 3, which was

Table 4. Extents of oxalic acids and benzenecarboxylic acids analyzed by GC-MS for the MEK extract prepared from Loy Yang coal

Relative extents (wt%)	Run 1	Run 2	Run 3
Oxalic acid	100	100	100
1 (BE)	5.6	20.4	7.5
2 (12BE)	2.6	17.9	9.5
3 (13BE)	3.2	8.9	15.5
4 (14BE)	1.7	5.8	3.7
5 (123BE)	7.3	25.0	13.9
6 (124BE)	21.8	146.6	105.1
7 (135BE)	6.8	56.5	29.2
8 (1245BE)	16.3	121.6	76.9
9 (12345BE)	29.6	277.3	112.1
10 (123456BE)	1.3	61.3	10.9
16 (1234BE)[a]	24.2	193.6	31.1
17 (1235BE)[b]	26.2	191.6	72.1

[a] 1234BE: 1,2,3,4-bezenetetracarboxylic acids.

[b] 1235BE: 1,2,3,5-bezenetetracarboxylic acids. All other abbreviations are the same as shown in Table 1.

Table 5. Extents of benzenecarboxylic acids analyzed by HPLC for the MEK extract prepared from Loy Yang coal

Relative extents (wt%)	Run 1	Run 2	Run 3
2 (12BE)	12.6	26.2	25.1
3 (13BE)	17.0	38.5	32.2
4 (14BE)	15.1	23.6	10.1
5 (123BE)	12.2	55.3	17.5
6 (124BE)	21.8	146.6	105.1
7 (135BE)	11.6	79.7	28.6
8 (1245BE)	25.6	92.2	35.0
9 (12345BE)	32.5	73.7	113.4

Relative extents are based on the values of No. 6 shown in Table 4. All abbreviations are the same as shown in Table 1.

prepared under the stronger oxidation conditions than others, showed better agreement between GC and HPLC analyses. This is probably due to the fact that under the stronger oxidation condition the influence of matrix within the oxidation product for the analysis of benzenepolycarboxylic acids is

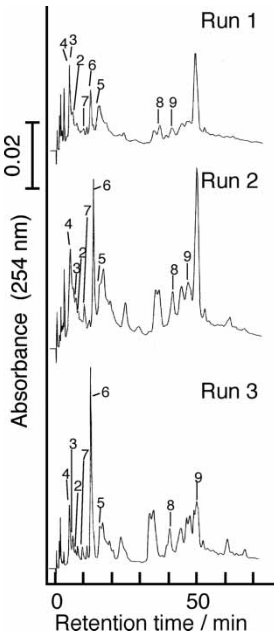

Figure 3. HPLC chromatograms obtained using solvent gradient for the MEK extract of coal oxidation products. Flow rate: 0.5 mL min^{-1}, 254 nm, 30°C, pH = 7.6, TMOABr: 3.5×10^{-3} mol kg^{-1}, methanol content for the linear gradient: 31.5% (0 min), 31.5% (15 min), 40.2% (35 min), 40.2% (75 min).

weaker than that under the mild oxidation condition. Thus, it is concluded that the HPLC analysis shown in this study is compatible to the conventional GC analysis. In addition, this separation condition can be used for the separation and isolation of a large quantity of coal oxidation products.

CONCLUSIONS

The separation of a mixture of 10 different benzenepolycarboxylic acids was succeeded simultaneously using quaternary ammonium salts and a solvent gradient method. The analytical data obtained by the present HPLC method is fairly consistent with that obtained by the conventional GC technique. Especially, the method was suitable for the coal oxidation products prepared under strong oxidation conditions. An optimum separation condition for the aromatic acids would be useful for more practical and large scale separation and also for the HPLC analysis. It is expected that this method was applicable for the practical separation and HPLC analysis of coal oxidation products as well as an analytical technique.

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