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Identification of Some Organic Compounds in Rain Water by Means of a Gas Chromatograph-Mass Spectrometer-Computer System

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Rain water (about 140 l), collected in suburban residential and downtown areas, was fractionated by column chromatography on Amberlite XAD-2 resin and silica gel. Trace amounts of organic compounds in rain water were identified by the use of a GC-MS-computer system combined with three-dimensional mass chromatography. Phthalate esters, polycyclic aromatic hydrocarbons, higher fatty acids and their esters, and other aromatic derivatives were identified with high reliability.

Keywords—analysis; rain water; organic compound; GC-MS; three-dimensional mass chromatography; computer; phthalate ester; polycyclic aromatic hydrocarbon; higher fatty acid; aromatic derivative

Introduction

Recently, long-range transport of air pollutants and acidification of rain water have caused serious environmental disruption in northern Europe and America.³⁻⁴⁾ In the case of acid rain, large amounts of SO_x and NO_x released into the atmosphere by combustion of fossil fuels result in the acidification of rain water. Various kinds of chemicals including inorganic oxides and organic compounds are also dispersed through the air, being adsorbed on the surface of fine particles or dissolved in fine water drops in the air, and then deposited on the ground surface when it rains. Accumulation of these pollutants from rain water during long periods may cause worldwide problems, affecting the remotest areas. The analysis of rain water has been carried out to identify materials relating to acidification of rain water or particular pollutants; inorganic compounds and organic acids in different types

of water were measured by ion chromatography,⁵⁾ and short-chain dicarboxylic acids and volatile organic acids in rain, fog, and mist were analyzed by capillary gas chromatography.^{6,7)} However, there are very few analytical results on a wide range of organic chemicals in rain water, probably because of difficulties in the analysis of environmental samples by conventional methods; those samples often show a high background and analysis is interfered with by co-existing multiple inorganic and organic compounds. A gas chromatograph-mass spectrometer-computer (GC-MS-COM) system was applied in environmental surveys combined with three-dimensional mass chromatography (TDMC) which has recently been developed in our laboratory.⁸⁻¹⁰⁾ A previous study verified the effectiveness of the system for environmental analysis.¹⁰⁾ In the present study, organic compounds in rain water were analyzed by using the GC-MS-COM system with TDMC, and many

organic chemicals were identified with a high reliability.

Experimental

GC-MS-COM System—The system consisted of a gas chromatograph-mass spectrometer (JGC 20 KP-JMS D100, JEOL, Tokyo) and an IBM system 7 computer (IBM, USA) as described previously.⁸⁾ The gas chromatograph was fitted with a glass column (2 mm×2 m) packed with Chromosorb W (80–100 mesh) coated with 3% OV-17. The temperatures of the injection port and column oven were 300°C and 100–300°C (10°C/min), respectively. The ionizing and accelerating voltages were 75 V and 3.0 kV, respectively. The total emission current was 300 μ A, and the ion source and separator temperatures were 160°C and 260°C, respectively. The main slit width and collector slit width were set at 300 and 100 μ m, respectively. The scan interval was 4–6 s and the sampling rate was 2000 points/s.

Three-Dimensional Mass Chromatography (TDMC) and Retrieval System—TDMC and identification of compounds were performed as described previously.^{8–10)} TDMC was used to clean up the contaminated spectrum at each scan time by removing fragment ion peaks which were not at the top of peaks in the mass chromatogram. The matching procedure in the retrieval system involves the confidence value (K), relative confidence value ($K\%$) and per cent contamination ($C\%$), with the criteria i) $K \geq 50$, ii) $K\% \geq 70$, iii) $C\% \leq 30$. The parameters were obtained by comparing the mass spectrum of the unknown compound with that in the Data Bank of EPA/NIH/MSDS (published in 1980) with the search algorithm described previously.^{8,11)} If the retrieval result satisfies all the conditions mentioned above, its match grade is A; if only two conditions, its match grade is B; and in other cases, its match grade is C as described previously.¹⁰⁾ Additional criteria can be used to give match grades such as A1, B1, C1, A2, B2, and C2; A1 means that the unknown is a compound with both the top K and top $K\%$ values among the estimated compounds, and A2 means that the unknown is a compound with either the top K or the top $K\%$ value. Therefore, A1 indicates the highest degree of

confidence and C2 indicates the lowest one for identification of a chemical, as described previously.¹⁰⁾

Rain Water—Rain water (about 140 l) was collected in suburban residential (in the campus of Osaka University) and downtown areas (on the rooftop of Osaka City Institute of Public Health and Environmental Sciences) of Osaka at the same period, using glass containers to avoid contamination with phthalate esters or their derivatives from plastic containers. Ten or fifteen glass containers with glass funnels (diameter 25 cm), covered with glass plates, were placed at the above two locations. The covers on the funnel were removed when it started raining and were put back after the rain had let up. The rain water in the containers was combined as soon as possible and kept at 4°C before fractionation. Chart 1 summarizes the procedure for fractionation of the rain water. The rain water was first applied to an Amberlite XAD-2 resin column (1.8×15 cm, flow rate 10 ml/min), and the adsorbed chemicals were successively eluted with 200 ml each of 0.1 M HCl, 0.1 M NaOH and diethyl ether. After elution with 0.1 M HCl and 0.1 M NaOH, the column was washed with distilled water until the eluate was neutral. The diethyl ether eluate was concentrated in a Kuderna-Danish evaporative concentrator and then applied to a silica gel column (1.8×13 cm) to fractionate it further into 13 sub-fractions by elution with the following solvents (each 200 ml), isooctane (sub-fra.

Chart 1. Procedure for Fractionation of Rain Water

No. 1); isooctane-benzene (1:1, No. 2); benzene (No. 3); benzene-CHCl₃ (1:1, No. 4); CHCl₃ (No. 5); CHCl₃-ethyl acetate (1:1, No. 6); ethyl acetate (No. 7); CHCl₃-methanol (20:1, No. 8; 10:1, No. 9; 5:1, No. 10; 2:1, No. 11; 1:1, No. 12) and methanol (No. 13). The HCl eluate and NaOH eluate fractions were both neutralized and extracted three times with 200 ml each of diethyl ether to prepare fra. I and II as shown in Chart 1. Fra. I and II were concentrated in a Kuderna-Danish evaporative concentrator.

Results and Discussion

Preliminary studies with the TDMC-GC-MS-COM system have suggested that sampling of a large amount of rain water and fractionation of the adsorbed chemicals on Amberlite resin into many fractions gave satisfactory results. Therefore, rain water (about 140 l) collected at the two stations was divided into many sub-fractions as shown in Chart 1.

The results of analysis of sub-fraction No. 9 from the suburban residential area is presented in Fig. 1; the total ion chromatogram (TIC) and chromatogram obtained by TDMC are shown in Fig. 1-a and 1-b, respectively.

TDMC provides automatic separation of unresolved peaks and elimination of broad and high background peaks in TIC. Many of the peak components with a relatively low intensity at each scan time on TIC can be analyzed in the TDMC system, but there is still the

Fig. 1. Analysis of Sub-fraction No. 9 from the Suburban Residential Area

a) Total ion chromatogram,
b) chromatogram obtained by TDMC.

TABLE I. Retrieval Results for Mass Spectra of Main Peaks in Fig. 1-b.

Peak position (scan No.)	Retrieval results	
	Match grade	Top <i>K</i> or <i>K</i> % compounds
50	B2	Tetraethylsilane (38, 76, 16)
82	B1	Hexanedioic acid bis (2-methylpropyl) ester (66, 55, 7)
	B2	3-Methylpentanedioic acid dibutyl ester (61, 58, 29)
118	B1	2-Methylpropanoic acid octyl ester (67, 71, 48)
129	B1	Phthalic acid butyl 2-methylpropyl ester (76, 91, 18)
147	A1	Hexanedioic acid dibutyl ester (84, 76, 25)
181	B1	(2 α , 3 β , 5 α)-Aspidofractinine-3-methanol (72, 55, 4)

The values in parentheses are *K*, *K*%, and *C*%, respectively. The list of retrieval results is limited to the compounds with match grades of A1, A2, B1, and B2.

technical difficulty that a peak component with very low intensity in a region of high background or close to a strong peak with the same m/z would be missed in this system, as discussed previously.¹²⁾ The compounds in the main peaks were automatically retrieved by the MPBM method based on a comparison of their mass fragment patterns with those of about 32000 authentic chemicals (Table I). The compounds from each peak in Fig. 1-b were identified from their match grades as follows; scan number 82 was estimated to be hexanedioic acid bis(2-methylpropyl) ester with a match grade of B1 or 3-methyl-pentanedioic acid dibutyl ester with a match grade of B2. Scan number 181 shows the highest intensity in this fraction and was identified as (2 α , 3 β , 5 α)-aspidofractinine-3-methanol.

The result of analysis of sub-fraction No. 7 from the downtown area is presented in Fig. 2. While the TIC gave a high background pattern containing some unresolved peaks (Fig. 2-a), the TDMC pattern gave many sharp and characteristic peaks (Fig. 2-b). Several compounds were identified with a high reliability in this fraction as follows; scan numbers 10, 43, and 50 were benzoic acid, phthalic acid, and 1 (3*H*)-isobenzofuranone, respectively, with

match grades of A1 (Table II). Many phthalate esters were also found in this fraction.

More than 200 compounds were detected from all of the fractions, but a majority of

Fig. 2. Analysis of Sub-fraction No. 7 from the Downtown Area

a) Total ion chromatogram,
b) chromatogram obtained by TDMC.

TABLE II. Retrieval Results for Mass Spectra of Main Peaks in Fig. 2-b

Peak position (scan No.)	Retrieval results	
	Match grade	Top <i>K</i> or <i>K</i> % compounds
10	A1	Benzoic acid (70, 75, 11)
	B2	Benzoic acid anhydride (47, 87, 15)
43	A1	Phthalic acid (70, 73, 5)
	A2	1,3-Isobenzofurandione (69, 76, 5)
50	A1	1(3 <i>H</i>)-Isobenzofuranone (55, 90, 23)
	A2	2-(Hydroxymethyl)-benzoic acid (53, 90, 23)
55	B1	3-Phenyloxiranecarboxamide (81, 79, 42)
118	B1	4-Formylbenzoic acid (51, 70, 45)
	B2	Phthalic acid butyl 2-methylpropyl ester (40, 91, 28)
169	B1	Phthalic acid dioctyl ester (60, 56, 10)
	B2	Phthalic acid diisooctyl ester (58, 61, 30)

The values in parentheses and the list of retrieval results are described in the footnote to Table I.

them were identified with low reliability (match grades of C1 or C2). Table III summarizes the retrieval results, limited to compounds with the highest match grades (over B1 level) at each separated scan peak position. The assigned

TABLE III. Summary of Retrieval Results for Organic Compounds in Rain Water

Compounds	Match grade
Group I	
17-Pentatriacontene	A2
2,6,11,15-Tetramethylhexadecane	B1
2,6,10,14-Tetramethylnonadecane	B1
Group II	
Decanedioic acid bis(2-ethylhexyl) ester	B1
Decanoic acid	B1
3,9-Diethyl-6-tridecanol	B1
1-Dotriacontanol	B1
Heptadecanoic acid ethyl ester	B1
Hexanedioic acid bis(2-methylpropyl) ester	B1
Hexanedioic acid dibutyl ester	A1
Hexanedioic acid dioctyl ester	A1
14-Methylpentadecanoic acid methyl ester	B1
2-Methylpropanoic acid octyl ester	B1
Nonahexacontanoic acid	B1
Octadecanamide	B1
9-Octadecenal	A1
1-Pentatriacontanol	B1
Tetradecanoic acid	B1
2,4,6-Trimethyldecanoic acid methyl ester	A2
Group III	
Not found over B1 level	
Group IV	
9,10-Anthracenedione	B1
(2 α ,3 β ,5 α)-Aspidofractinine-3-methanol	B1
Benzenemethanol	B1
Benzoic acid	A1
1,1'-Biphenyl	A1
1,2-Dihydroacenaphthalene	B1
13A,3A-(Epoxyethano)-1H-indolizino derivative	B1
4-Formylbenzoic acid	B1
4-Methyl-3(2H)-benzofuranone	B1
1(3H)-Isobenzofuranone	A1
5-Methyl-1(3H)-isobenzofuranone	B1
1-Methoxy-4-nitro-benzene	B1
5-Methylprimidine	B1
1-Methyl-1-propylpentyl-benzene	A2
9,10-Phenanthrene-dione	B1
3-Phenyloxiranecarboxamide	B1
1-Phenyl-1-penten-3-one	B1
3-Phenyl-2-propenal	B1

TABLE III. (continued)

Compounds	Match grade
Group V	
Phthalic acid	A1
Phthalic acid butyl 2-methylpropyl ester	B1
Phthalic acid dibutyl ester	B1
Phthalic acid diethyl ester	A1
Phthalic acid diisooctyl ester	A1
Phthalic acid dioctyl ester	B1
Group VI	
Phosphoric acid tributyl ester	B1

Group I consists of higher saturated and unsaturated hydrocarbons; Group II, higher fatty acids, esters, alcohols, amides, and aldehydes; Group III, aliphatic and hetero-aliphatic compounds; Group IV, aromatic derivatives; Group V, phthalates; Group VI, others.

The list of results is limited to the compounds with high match grades (over B1 level) at each separated scan peak position.

compounds were classified into six groups as follows. As higher saturated and unsaturated hydrocarbons (group I), 17-pentatriacontene and other saturated hydrocarbons were found with match grades of A2 or B1 level. Hexanedioic acid esters, 9-octadecenal, and 2,4,6-trimethyldecanoic acid methyl ester were found as group II compounds with match grades of A level. As aromatic derivatives (group IV), an anthracene derivative, benzene and phenol derivatives, benzofuranone, isobenzofuranone, pyrimidine, and (2 α , 3 β , 5 α)-aspidofractinine-3-methanol were found with match grades of over B1 level. Various types of phthalate esters were found with A1 level (in group V). Since the rain water was concentrated at about 50°C *in vacuo* in the fractionation, volatile chemicals were not subjected to analysis in this survey.

Many organic compounds have been detected in the atmospheric environment,¹³⁾ and in particular, numerous polycyclic aromatic hydrocarbons (PAH) were found in airborne particles in studies concerned with mutagenicity or carcinogenicity.¹⁴⁾ In Japan, some selected organic chemicals (557 compounds) have been surveyed extensively in water, mud, and some fishes

for the last 10 years, and some of them have also been measured in the atmosphere.¹⁵⁾ In those surveys, 26 chemicals, including di (2-ethylhexyl)-adipate, methylnaphthalene, dichlorodifluoro-methane, chlorobenzene, trihalomethanes and phthalate esters, were detected in the atmosphere. These or their derivatives were also found in the rain water, even though the match grades varied from case to case, so it appears that chemicals in rain water do reflect the state of air pollution. As expected, various phthalate esters and PAHs such as anthracene, acenaphthalene and phenanthrene derivatives were found in rain water. In this study, benzo[*a*]pyrene, a typical air pollutant, was not found though structurally related compounds such as anthracene and phenanthrene derivatives were found with match grades of B1 level. The reason why benzo[*a*]pyrene was not detected is not known. The analysis of organic

chemicals in rain water showed little qualitative difference between suburban residential and downtown areas (these are about 20 km apart), but changes in the relative intensity of some chemicals were observed in corresponding fractions from these areas (data not shown). While atmospheric phenomena should be considered in the evaluation of air pollution, the present results imply the general patterns of chemicals in the atmosphere of downtown and adjacent suburban areas.

Although the present study concentrated on a qualitative analysis, we have confirmed the availability of the TDMC-GC-MS-COM system for environmental surveys and have obtained useful information about organic chemicals in rain water. Application of this system to examine field samples collected systematically should yield useful data for the evaluation of environmental pollution.

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