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Identification of emission sources of organic matter that decalcifies cement concrete and generate alcohols and ammonia gases

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Abstract

In this study, the emission sources of various types of airborne organic matter, which deteriorates cement concrete by penetrating into it together with moisture, were identified using high-performance liquid chromatography and gas chromatograph mass spectrometer. As a result, it was revealed that the types of organic matter contained in decalcified cement concrete were almost the same as those found in total suspended matter in the air, and that they were primarily being emitted as particles of exhaust from diesel vehicles and radial tires used in summer. Such organic matter includes substances suspected as having endocrine disrupting properties. Hydrolysis occurs when these substances penetrate into a highly alkaline cement concrete, and leads to deterioration of cement concrete and the release of particular kinds of alcohols and ammonia gases, which pollute indoor air and can cause sick building syndrome.

Key words: cement concrete, decalcification, black organic matter, alcohol, ammonia gas

1. Introduction

Since total suspended matter (TSM) in the atmosphere has a significant influence on human

health and natural environment, it is becoming a serious problem throughout the world [1] and [2]. TSM includes minute particles of organic matter 2.5 μm or smaller in diameter and suspended particulate matters (SPM) (black carbon particles), which are thought to be harmful to human health when inhaled [3]. It is generally believed that organic matter in TSM mainly consists of diesel exhaust particulate (DEP) and soot emitted from chimneys and factory smokestacks [4] and [5]. The authors tried to analyze the contribution of DEP, radial tires used in summer and asphalt to TSM using linear model and chemical analysis[6], not chemical mass balance and other methods[4],[5] and [7]. It was then reported that the ratio of DEP to TSM was extremely high in black organic matter emitted from these three sources of TSM.

It was also reported that the anion type surfactant in windshield washer fluid of automobiles in the air reacts chemically with cement concrete and decalcifies it[8]. It will be splashed into the air by the tire of automobiles. We observed the decalcified cement concrete in a flyover covered with tiles at 8 m height above the surface of a road. Since anion type surfactant splashed from the road below does not spatter the structure surface, we assume that the surfactant penetrates into the cement concrete through "aspiration of cement concrete". The aspiration phenomena of cement concrete was examined in laboratory. The anion type surfactant on the surface of asphalt pavement on concrete bridge (asphalt layer: 4 cm + 4 cm, cement concrete: 4 cm) easily penetrated into the cement concrete of bottom layer, under the time difference of temperature change of pavement surface and bottom of cement concrete, and decalcified the cement concrete[9].

In general, it is considered that maximum depth of decalcification of cement concrete due to carbon dioxide is 5 mm for 20 years[10]. However, the maximum depth of decalcified cement concrete in the fields near heavy duty roads, can be 15 cm or more in 30 years after the construction. The average depth of decalcified cement concrete (30 years later) in Great Hanshin Kobe Earthquake in Japan in 1995 was 3-4 cm for various cement structures such as piers, buildings, bridges, and small pieces of cement concrete broken by earthquake near heavy duty roads. Such decalcification was observed even inside (20 cm or more from surface) of steel bars[8]. We call the phenomenon “disaggregation” of cement concrete, and anion type surfactant in windshield washer fluid of automobiles was also detected in those decalcified cement concrete.

Recently, certain kinds of alcohols (2-ethyl-1-hexanol (2E1H) and 1-butanol), which are thought to be a cause of sick building syndrome, were detected at high concentrations in buildings in Japan[11],[12]. It is believed that those alcohols are generated between the concrete surface and the carpeting materials, such as new carpets and adhesives. But even if those materials are got rid of, the alcohols continue to emit in the buildings. It is also known that ammonia gases, which are generated from aggregates and cement in the cement concrete of newly constructed art museums, cause deterioration of the linseed oil found in oil paintings[13].

The objectives of this study therefore are as follows: (1) to investigate where the organic matter in decalcified cement concrete come from; (2) to clarify what kinds of organic matter harmful to cement concrete exists; (3) to examine generation mechanism of substances such

as 2E1H and ammonia gases through “aspiration of cement concrete”.

Based on the test results, it was suggested that cement concrete absorbs the air containing organic matter harmful not only to cement concrete but also possibly to human health, and that the organic matter decalcified cement concrete and/or generated various alcohols and ammonia gases.

2. Experiment

(1) Samples

a) Decalcified cement concrete

Samples of decalcified concrete were collected from the center lane (unrepaired and not included with calcareous aggregate[14]) of an express highway with a traffic volume of 40 000 vehicles/day/threelanes. The highway was constructed 30 years ago in Osaka. Phenolphthalein liquid was sprayed on the decalcified specimens of the highway concrete, but they were not tinted pink. This means that the pH of the concrete specimen decreased from 12 to 10 or smaller (decalcification of cement concrete). Samples of decalcified cement concrete were milled into powder finer than 0.074 mm in grain size.

b) TSM

Decalcified samples (100 samples or more) of limestone and cement concrete were collected in Belgium, France and Japan, and ^1H NMR (Nuclear Magnetic Resonance) test performed for organic matters in those samples. The same patterns of ^1H NMR spectrum for those samples were obtained. Then, we assumed that the pattern of air pollution in each country is the same.

Therefore, TSM samples were collected for 8 days in July 1998 on the roof of a six-story building of the Faculty of Engineering, Hokkaido University, in Sapporo, which is located 1 000 km apart from Osaka, using a high-volume sampler (HVC-1000N: Shibata Scientific Technology, Pallflex 2500QAT-UP, quartz fiber filter, 23.5 × 17.5 cm, 1000 l/min.). Sapporo is a city in the northern part of Japan, and Hokkaido University is located 1 km away from the city center.

c) DEP

DEP samples were collected at the Japan Automobile Research Institute in Tsukuba, using a dilution tunnel (Horiba, DLT-24150W) and an air filter.

d) Tire

Small samples were shaved off from a new summer radial tire commercially available for automobiles in Japan.

e) Asphalt

Straight asphalt (penetration: 80-100) commonly found in Japan was used.

f) Cement paste

1. Normal Portland cement C (Normal C)
2. High-Early-Strength cement B (Early B)
3. High-Early-Strength cement A (Early A)
4. High-Early-Strength cement C (Early C)
5. Blast furnace cement C (Blast C)
6. High-Early-Strength cement C+AE water-reducing agent (weight of cement x 0.5 %)

(Early C+AE)

Distilled water of 50 % for the weight of the cement was added in all cement and hardened cement paste samples were crushed with hammer. Those samples were sieved with 0.074 mm sieve as a following test sample.

Curing time for Normal Portland cement and high-early-strength cement was 28 days and seven days respectively and they were adjusted the curing days in order to conduct test at the same day after hardening.

g) AE water-reducing agent

A lignin sulfonate acid salt + polyol complex (some kinds of anion type surfactant) was used.

(2) Analytical Method

a) HPLC

Samples of decalcified cement concrete, TSM, DEP, tire, and asphalt, were at first dissolved in benzene methanol solution (ratio of volume: 1:1) and then dissolved again in normal hexane in order to extract soluble compounds[15]. The compounds (oil components) obtained, after the latter extractions were divided into saturated hydrocarbons, one-ring aromatic compounds, two-ring aromatic compounds and polar compounds using HPLC (Nippon Bunkou, TRI-Rotor with ZORBAX-BP-NH₂, column with inner diameter 10 mm, length 250 mm, speed of chloroform of solution: 5.0 ml/min.)[8]. Each compound with the exception of polar compounds was gathered by the aid of RI and UV detectors, and polar compound was collected by chloroform.

b) GC-MS

Organic matter including the polar component obtained from decalcified cement concrete, in TSM, DEP, the tire, and asphalt samples was identified using GC-MS (JMS-AX-500, column with inner diameter 0.32 mm, length 30 m, column temperature: 50-280 °C).

c) Double-cylinder-chamber method

About 10 g samples of the powdered cement paste were put in a stainless container (inside diameter 54 mm x 40 mm in depth in 92 cm³ in capacity). The surface of samples was flatted with spatula. Di-(2-ethylhexyl) phthalate (DEHP) (special grade) of 0.4 g, which is an oily substance, was dispersed on the surface of the cement samples. Thereafter, a stainless container was covered up and kept in 30 °C in an incubator.

2E1H concentrations emitted from powdered cement paste were measured by the double-cylinder-chamber method [16]. The double-cylinder-chamber was a circular, polished stainless lid with an inner diameter of 124 mm and a volume of 1.4 L (GL Sciences, Japan). The sample was placed in the inside of double-cylinder-chamber.

The chamber was supplied with clean humidified air (relative humidity: 50 %) with a flow of 450 mL/min.. 2E1H in the air from the chamber was adsorbed on a charcoal tube (Jumbo type, Sibata Scientific Technology, Japan) connected to a sampling pump (SP 308 Dual, GL Sciences, Japan) and a flow of 100 ml/min. was drawn through a charcoal tube for 10 minutes. The charcoal tube had two separate layers of activated charcoal: the front layer contained 400 mg of activated charcoal and the rear layer contained 200 mg. The rear layer employed to confirm the breakthrough of 2E1H in the front layer. The absorbent in the charcoal tube was transferred into

vials containing 4.0 ml of CS₂ for the front layer and 2.0 ml of CS₂ for the rear layer. The vials were then stoppered tightly, shaken, and placed at room temperature for 2 hours. They were centrifuged for 10 min. at 3000 rpm. One ml of a supernatant, to which 5 µl of an internal standard solution (200 µg/ml, toluene-d₈, Aldrich, USA) was added, was then transferred into auto injector vials for analysis by a gas chromatograph with a mass spectrometer (GC-MS). The GC-MS (5980 Series II/5971A, Hewlett Packard, USA) was equipped with a 60 m × 0.25 mm i.d. capillary column coated with a 1.5 µm film of NB-1 (GL Sciences, Japan). The GC oven temperature was first maintained at 45 °C for 5 min.; it was then programmed to 300 °C at 10 °C/min., and maintained at 300 °C for 7 min.. The analysis was performed with a helium flow rate of 0.9 mL/min. under a selected-ion monitoring mode targeting 2E1H.

The calculation of the emission rate of volatile organic compounds (VOC) was as follows:

$$E = C \times V \times (1/L)$$

where

E: emission rate (µg/hr·m²), C: airborne VOC concentration in double-cylinder-chamber (µg/m³),

V: number of air change per hour (frequency/hr), L: loading factor (constant, 12.56 m²/m³)

A background air sample was taken on every measurement day. The double-cylinder-chamber was placed on an aluminium foil (50×50 cm) laid on the floor and a flow of clean humidified air was passed through the chamber with the same flow rate, time and sampling system as in measuring emissions from the cement paste samples. The result from this sample is compensated

for the actual background.

In order to determine the background amount of 2E1H in a charcoal tube, three unused charcoal tubes were measured, as described above. The background amounts per charcoal tube were less than detection limit.

The phase equilibrium method was used to determine the desorption efficiency of 2E1H collected on the adsorbent [17]. The adsorbent (400 mg) was slowly added to a 4 ml solution of 2E1H (500 ng/ml: CS₂). By the method used for analyzing the samples, the solution was again analyzed, and the desorption efficiency was calculated by dividing the resulting concentration by that obtained from the original solution. The desorption efficiency of 2E1H was 70 % with the coefficient of variation of 2.5 %.

For the reproducibility test, three powdered cement pastes containing DEHP were simultaneously prepared and stored for 7 days at 30 °C in the incubator. 2E1H concentrations emitted from the samples were measured by the method used for analyzing the samples. The coefficient of variation in the amount of 2E1H amounts was 6.6 %.

3. Results and Discussion

(1) Determination of emission sources of organic matter

Fig. 1 shows the GC-MS spectra of the extracted polar component of decalcified cement concrete and TSM separated by HPLC. It can be seen from the figure that the two spectra are very similar to each other. Table 1. lists the results of GC-MS identification of organic matter in the polar components of decalcified cement concrete, TSM, DEP, the tire and

asphalt samples, separated by HPLC. The detected compounds in decalcified cement concrete were Di-n-butyl phthalate (DBP), Di-(2-ethylhexyl) phthalate (DEHP), Di-octyl phthalate (DOP) and other phthalic acid esters, Palmitoleamide ($C_{15}H_{29}CONH_2$), Palmitamide ($C_{15}H_{31}CONH_2$), Oleamide ($C_{17}H_{33}CONH_2$), Stearamide ($C_{17}H_{35}CONH_2$) and other amides, Octadecane ($C_{18}H_{38}$, normal paraffin) and 2,2,4-Trimethyl-1,3-Pentanediol Di-isobutylate (TMPDIB). The organic matter extracted from TSM was also detected in decalcified cement concrete. This means that organic matter in decalcified cement concrete, i.e. normal paraffin, amides and phthalic acid ester, contains almost the same components as in TSM. It is thus suggested that cement concrete absorbs airborne organic matter together with moisture as it “breathes” like animals and plants when the time difference between surface and bottom temperature exists [9]. The components of organic matter detected in TSM were the same as those in the tire samples and DEP, except for DOP, which was detected only in the tire. Since normal paraffin ($C_{16}H_{34}$, $C_{17}H_{36}$, $C_{22}H_{46}$, $C_{42}H_{86}$) contained in asphalt was not found in TSM, it is presumed that organic matter in the tire (under 2.5 μm) samples and DEP was mainly released into the atmosphere and such organic matter penetrated into cement concrete through “aspiration action of concrete”. While DBP, DEHP and other phthalic acid esters are often used as plasticizers in traffic painting, they have been suspected as having endocrine disrupting properties in Japan [18]. The dose-response effects and risks of these substances have also been assessed in the United States [19], EU[20], and in other countries.

(2) Generation of 2E1H from cement paste

Six kinds of powdered cement paste samples (2 g) were heated at 110 °C for 24 hours. In order to measure the water content, the sample weights were compared between before and after heating. Those results were shown in Table 2.

Cement paste sample (Early C +AE) to which AE water-reducing agent was added had higher water content than others, and emission of 2E1H was abnormally large in the early days (Table 3.). The results suggested that AE water-reducing agent increased the moisture absorption of the cement, which resulted in increased DEHP absorption into the cement paste and led to larger emission of 2E1H. It was likely that hydrolysis of DEHP increased by the existence of AE water-reducing agent, anion type surfactant.

As for the above-mentioned results, water content is constant, but the same result (water content of the normal cement concrete is regarded as around 10 %) is obtained even if water content 10 % is increased.

A phenomenon the same as the “aspiration” action that occurred with cement concrete in the above-mentioned experiment was confirmed in the cement paste sample.

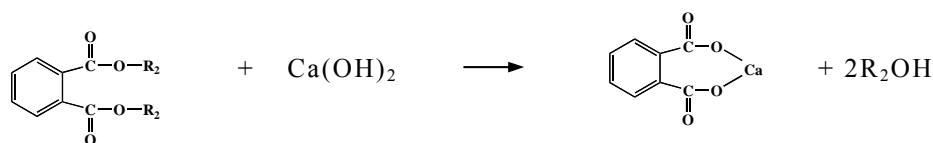
As a result, because harmful organic substance is easily taken into the inside of the cement paste with the existence of AE reducing agent by the aspiration action, it is considered that it neutralizes the cement concrete containing AE water-reducing agent (anion type surfactant). It means that the organic matter such as DEHP, which is harmful to cement concrete, deteriorates it even if the organic matter does not have a direct contact with it.

(3) Substances produced by reaction between organic matter and cement concrete

It was found that phthalic acid esters, amides and normal paraffins in the atmosphere were

absorbed by cement concrete. Of these types of organic matter, phthalic acid esters, TMPDIB and amides are thought to cause hydrolysis of ester, if they penetrate into a strong alkaline substance (pH = 12 to 13), such as cement concrete. The reactions of calcium hydrate and phthalic acid ester, TMPDIB and amides in cement concrete are expressed by the equations below.

Phthalic acid esters

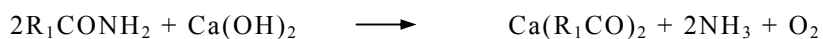


where alkyl moiety: $\text{R}_2 = \text{C}_4\text{H}_9$ (for DBP), C_8H_{17} (for DOP, DEHP)

TMPDIB



Amides



where alkyl moiety: $\text{R}_1 = \text{C}_{15}\text{H}_{29}$ (for Palmitoleamide), $\text{C}_{15}\text{H}_{31}$ (for Palmitamide), $\text{C}_{17}\text{H}_{33}$ (for Oleamide), $\text{C}_{17}\text{H}_{35}$ (Stearamide)

When DEHP or DBP or DOP (each 0.05 g, 10 000 ppm) was added to the crushed powdered

sample of fresh cement paste (Normal Portland cement C, 5 g) at ambient temperature respectively, 2E1H or butanol or octanol, which was generated from DEHP or DBP or DOP respectively, was also found in the sample using GC-MS. When TMPDIB (0.05 g, 10 000 ppm) was also added to the sample (5 g) at ambient temperature, 2,2,4-trimethyl-1,3-Pentanediol which was generated from TMPDIB, was also found in the sample using GC-MS. It was thus found that when phthalic acid esters and TMPDIB reacted, hydrolysis occurred and caused a variety of alcohols to be generated. Here, special attention must be paid to 2E1H. In Europe and the United States, 2E1H is recognized as an indoor air contaminant released from carpet linings and other PVC products [21-25], and its connection with symptoms of asthma [26] and nose and eye irritation [27] has been pointed out. In Japan, 2E1H is also known as a substance that causes irritation of the eyes, nose and throat, nausea and other symptoms of sick building syndrome in newly constructed and renovated buildings, and it is presumed that 2E1H is generated by hydrolysis caused by DEHP contained in floor linings and adhesives and concrete slabs[11]. This study, however, revealed that 2E1H causing sick building syndrome[27] was generated not only from organic matter in carpets and adhesives, but also from airborne organic matter that penetrated into cement concrete after curing. It was thus found that DEHP and other phthalic acid esters suspected as having endocrine disrupting properties not only accelerate the neutralization of cement concrete, but also initiate reaction that have secondary adverse effects on humans.

Ammonia gas was detected by measuring the pH of the gas that was generated by reactions of oleic amide and calcium hydrate in warm water (60 °C). The generation of ammonia gas

was detected as the pH paper changed from neutral to alkaline. In recent years, it has been reported that ammonia gases generated from aggregates and cement contained in cement concrete are causing the deterioration of linseed oil used in oil paintings in newly constructed art museums [13]. It has also been reported that the addition of amines as antifreezing agents in cold regions also causes large amounts of ammonia gas to be generated in cured cement concrete in the same way as in the case of amides [28], and that ammonia gas generated by urea-compound fluidizers added to self-leveling mortar causes sick building syndrome [29]. It was, however, confirmed in this study that the same phenomenon could occur as the secondary of reaction between cement concrete and airborne amides that penetrated in it.

4. Conclusion

In this study, DEP, radial tires used in summer and asphalt in asphalt pavements were identified as emission sources of organic matter that decalcifies cement concrete. It was also found that such organic matter causes the neutralization of cement concrete and the release of alcohols and ammonia gases that cause sick building syndrome, when they spread in the air and penetrate into cement concrete through “aspiration”. Since phthalic acid esters are used in large amounts as plasticizers for PVC, tires and traffic paints throughout the world, this phenomenon may be occurring not only in Japan, but also on a global scale. In addition, since surfactants and esters are mixed into concrete as additives, it is highly possible that this phenomenon is caused not only by airborne organic matter and other external factors, but

also by organic matter existing inside cement concrete. It is thus thought that this phenomenon is making the service lives of cement concrete structures extremely short, and may change the conventional concepts regarding damage to cement concrete and limestone structure[24]. As civil engineers, we have had opportunities to deal with various areas of study, including those that could address possible endocrine disrupting properties and sick building syndrome[31], in our studies of the deterioration of civil engineering structures. Such studies, linking civil engineering and medical science, will be important in the future.

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Table Captions

Table 1. Main chemical components of polar compound in decalcified cement concrete, TSM, DEP, tire and asphalt

Table 2. Water content (%) in powdered cement paste samples

Table 3. Time change of the quantity of emission of 2E1H (mg/hour/m³)

Figure Caption

Fig.1. GC-MS spectra of the polar compounds in decalcified cement concrete and TSM

Table 1. Main chemical components of organic compounds in Decalcified concrete, TSM, DEP, tire and asphalt

Sample	Phthalic acid Ester	R ₁ ⁵ CONH ₂ (Amide)	Hydrocarbon
Decalcified	DBP ¹⁾ , DEHP ²⁾ ,	C ₁₅ H ₂₉ , C ₁₅ H ₃₁ ,	C ₁₈ H ₃₈
Cement Concrete	DOP ³⁾ , TMPDIB ⁴⁾	C ₁₇ H ₃₃ , C ₁₇ H ₃₅	
TSM	DBP ¹⁾ , DEHP ²⁾ ,	C ₁₅ H ₃₁ , C ₁₇ H ₃₃ ,	C ₁₈ H ₃₈
	DOP ³⁾	C ₁₇ H ₃₅	
DEP	DBP ¹⁾ , DEHP ²⁾ ,	C ₁₅ H ₃₁ , C ₁₇ H ₃₃ ,	C ₁₈ H ₃₈
		C ₁₇ H ₃₅	
Tire	DBP ¹⁾ , DEHP ²⁾ ,	C ₁₅ H ₃₁ , C ₁₇ H ₃₃ ,	C ₁₈ H ₃₈
	DOP ³⁾	C ₁₇ H ₃₅	
Asphalt		C ₁₇ H ₃₃ , C ₁₇ H ₃₅	C ₁₆ H ₃₄ , C ₁₇ H ₃₆ , C ₂₂ H ₄₆ , C ₄₂ H ₈₆

1)DBP: Di-n-butyl phthalate, 2)DEHP: Di-2(ethylhexyl)phthalate,

3)DOP: Di-octyl phthalate, 4)TMPDIB: 2,2,4-Trimethyl-1,3-Pentenediol Di-isobutylate,

5)R₁: Alkyl moiety

Table 2. Water content in powdered cement paste samples

Sample No.	1	2	3	4	5	6
	Normal C	Early B	Early A	Early C	Blast C	Early C+AE
Weight of sample (g)						
Before heat	2.18	2.12	2.12	2.11	2.11	2.13
After heat	2.09	2.03	2.02	2.00	2.00	1.98
Quantity of water (g)	0.09	0.09	0.10	0.11	0.11	0.15
Water content (%)	4.1	4.2	4.7	5.2	5.2	7.0

Table 3. Time change of the emission rate of 2E1H (mg/hour/m²)

Sample No.	1	2	3	4	5	6	
	Normal C	Early B	Early A	Early C	Blast C	Early C+AE	
Days	0	0	0	0	0	0	
	1	9.0	5.7	12.6	13.7	16.8	29.9
	7	23.0	12.0	26.9	31.2	19.6	32.4
	14	25.1	15.7	29.7	26.7	20.9	38.4
	28	28.4	17.3	25.8	29.6	26.9	25.7
	42	30.9	23.4	38.8	33.9	30.6	31.8
	56	33.8	31.8	49.4	34.0	31.6	32.9
	92	32.0	21.7	41.0	33.9	20.9	21.1

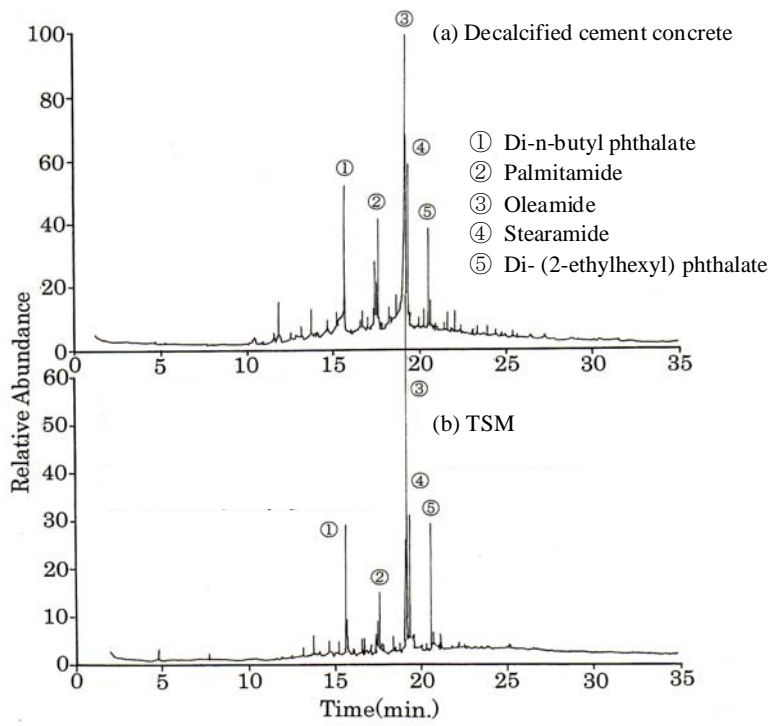


Fig.1. GC-MS spectra of the organic compounds in decalcified cement concrete and TSM