DEVELOPMENT OF A MICROANALYSIS METHOD OF PHTHALATE ESTERS IN INDOOR AIR AND ITS APPLICATION TO PRACTICAL MEASUREMENT

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ABSTRACT
The authors have developed a microanalysis method for the purpose of elucidating the actual form(particulate or gaseous) of phthalate esters(P.E.) present in indoor air and the particle size distribution and individual exposure amounts. In this study, a method of sampling was used layering 2 sheets of filter material different in collecting property and the method of analysis by GC/MS was established. The technique was applied to the measurement of indoor air it became clear that the P.E. were always present in both the particulate form and gaseous form. And, it was also made clear that in the particle size distribution the concentration of micro particles not more than 2.5 μm tended to be high.

INDEX TERMS
Determination method, Phthalate ester, Indoor air, GC/MS.

INTRODUCTION
Phthalate esters (P.E.) are used for plasticizers for plastics, vinyl cloths, water pipes, floorings, feeding bottles, coatings and the others including industrial products, building materials and household utensils, and thanks to its chemical properties, many useful chemical products are realizable, greatly contributing to improvement of our living standard. However, P.E. are eluted from those products and are dispersed into the air causing the river and air pollution, and endocrine disrupting effects upon wild animals and humans, in particular upon their reproductive functions, are feared. The Ministry of the Environment of Japan has selected 74 substances which are suspected to have endocrine disrupting action and has begun administrative measures to combat these effects. As part thereof, a survey of P.E. in river waters and atmosphere has begun.

Okubo and Seto are reported with the measurement result of P.E. in offices and homes in Tokyo. The authors have developed a microanalysis method of P.E. in indoor air and have reported the results of the on-site surveys which used this method. The paper shows that we made the actual conditions clearer with a more sensitive analysis as well as by measuring P.E. by form (particulate and gaseous) and particle size using this method. As a result, it was made clear that particulate and gaseous forms of this substance were both always present and that, in particle size distribution the proportion of micro particle not more than 2.5 m (PM2.5) was large.

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EXPERIMENTAL METHOD

Measurement substances and reagents

Among the P.E., the following 11 substances were made the subjects for analysis:
Dimethyl phthalate (DMP), Diethyl phthalate (DEP), Diallyl phthalate (DAP), Dipropyl phthalate(DPP), Diisobutyl phthalate (DIBP), Di-n-butyl phthalate (DBP), Butyl benzyl phthalate (BBP), Di-n-hexyl phthalate (DHP), Dicyclohexyl phthalate(DCHP), Di-octyl phthalate (DCP), Di-nonyl phthalate (DNP)
Internal standard solution were used of DEP-d, DBP-d and DOP-d.

Collector

Glass Fiber Filter: 47 mm, AE, made by Gelman,
Quartz Fiber Filter: 2500QRT-UP, made by Pallflex
Empore Disk C18 Filter(henceforth, abbreviated DiskFilter):Octadecyl(C18) 47 mm, made by 3M
Carbon Disk Filter: 47 mm, made by 3M

Apparatus

GC/MS: Model QP-5050, made by Shimadzu
Low-noise Type Cascade Impactor (NILU Impactor): Made by Tokyo Dylec Co., Ltd.

Sampling

Sampling of respective forms(particulate and gaseous)

In the case of sampling of particulates and gas, the quartz fiber filter was first attached to the filter holder and then the Empore Disk C18 was attached to the filter holder, and sampling was made at the flux of 5 L/min for 2 days. The sampling point was at the center of room about 1.2 m above from the floor. The matter trapped by the quartz glass fiber of the first stage was defined to be particulate and that by the Empore Disk C18 to be gaseous. The filters that respectively trap the particulates and the gas were used as the samples for analysis of the two forms.

Sampling by particle size

An air sampler equipped with a NILU impactor was mounted with a quartz fiber filter,and the sampling point was set at a point in the center of room about 1.2 m above from the floor, and sampling was made at the flux of 3 L/min for 7 days.

Analytical procedure

Particulate matter

The filter for analysis was torn up finely and put in a stoppered test tube. 10 ml of the mixture solvent was poured in and left for 30 minutes. Ultrasonic extraction was done for 10 minutes, the supernatant fluid was transferred to a centrifugal separating tube (10ml) and centrifuged in a refrigerated centrifuge at 3000 rpm for 10 minutes (0ºC). Then, 1 ml of the supernatant fluid was removed, 20 μl of the 3-species mixed internal standard solution (200 ng of each internal standard substance, DEP-d, DBP-d, DOP-d) was added and mixed, 1 μl of this solution was transferred into the GC/MS where it was analyzed.

Gaseous matter

The analysis operation is made in conformity with particulate matter

RESULTS AND DISCUSSION

Preparation of the filter

When collecting and analyzing P.E. in the air, many contaminating factors such as contamination of the trappers, contamination during the analysis operation and the laboratory atmosphere are conceivable, and they are obstructions to accurate analysis. Therefore, a test of methods to reduce the filter blank, the top among the contaminating factors was made.
In the section, the quartz and glass fiber filters were selected for trapping of particulate matters and the Empore Disk C18 and Carbon Disk Filter for trapping of gaseous matters, and measurement of blanks was made according to the analytical procedure. As a result, it was found that every filter was high in blank and that the filters could not be used for the actual measurement as they were. Thus, a test was made of cleaning methods to reduce the blank of each filter. For the quartz and glass fiber filters for trapping of particulates, a method of treatment was tried in which the filter was heated for 3 hours in an electric furnace at 250ºC while passing nitrogen through the furnace. On the other hand, for the Empore Disk Filter and Carbon Disk Filter for trapping of gaseous matters, a ultrasonic cleaning method was used using acetone, dichlorobenzene and the mixture solvent (acetone: toluene = 7: 3). As a result, it was found that the heating treatment method was very effective in reduction of the blank for the cases of the quartz and glass fiber filters and, for the cases of the Empore Disk C18 and Carbon Disk Filter, the use of dichlorobenzene and the mixture solvent.

Rate of recovery

The standard solution of P.E. was added to the filters of glass fiber, quartz fiber, Carbon Disk and Empore Disk C18, the analysis operation as in method was made, and a recovery test was made. As a result, as shown in Table 1, recovery of more than 90 % was obtained for each P.E. when the mixture solvent was used for extraction in the cases of the glass fiber filter, quartz fiber filter and Carbon Disk Filter. Accordingly, the mixture solvent was selected for the extraction solvent.

Table 1 Recovery test of phthalate esters

	Recovery (%)		
Substances	Quartz fiber filter	Glass fiber filter	Carbon disk filter
DMP	94.1	91.1	91.1
DEP	102.9	100.1	100.2
DAP	109.4	98.8	99.5
DPP	97.3	94.1	98.6
DIBP	97.0	96.6	97.6
DBP	98.0	92.4	94.4
BBP	99.7	90.1	94.2
DHP	97.7	97.0	98.6
DCHP	103.7	99.9	99.4
DOP	98.6	90.4	94.3
DNP	101.8	91.2	94.6

500 ng phthalate esters was added into the each filters

Actual measurement test

This method was used for actual measurement of the P.E. in the habitation environment. As a result, as shown in Fig.1, DBP and DOP showed higher particulate concentration and DMP and DEP higher gas concentration. And, as shown in Fig.2, it was made clear that, in the

particle size distribution, the concentration of fine particle of not more than 2.5 μm tended to be high.

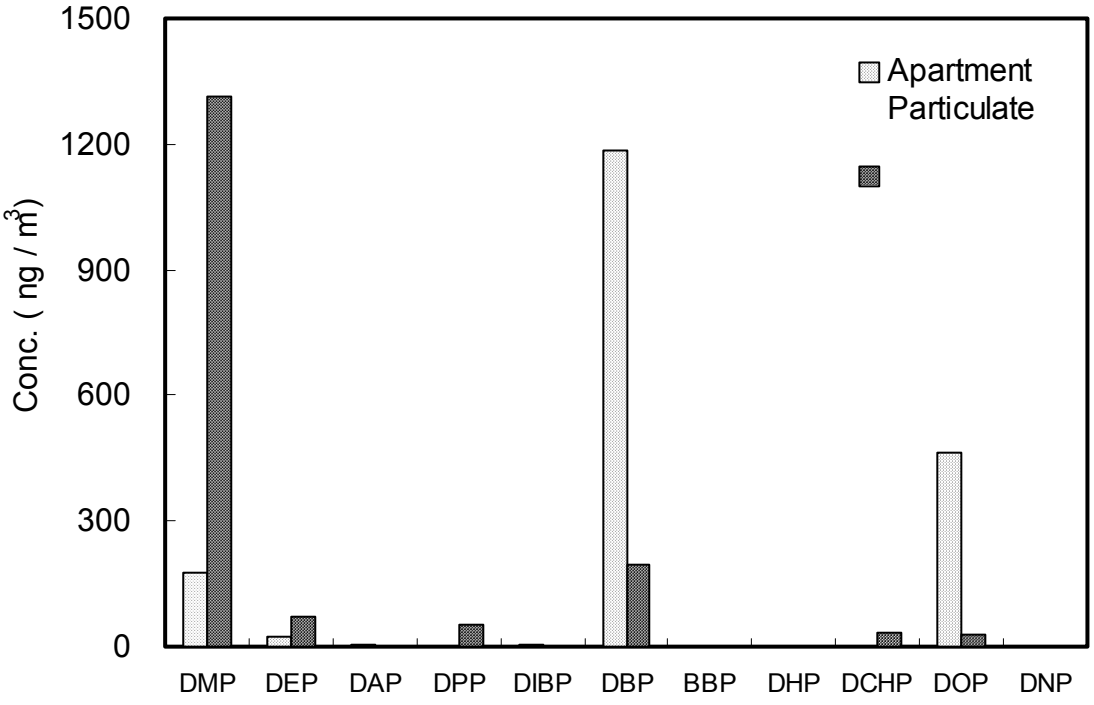

Figure 1. Example of measurement result of particulate and gaseous phthalate esters in indoor air sampling:5L / min x 2 days

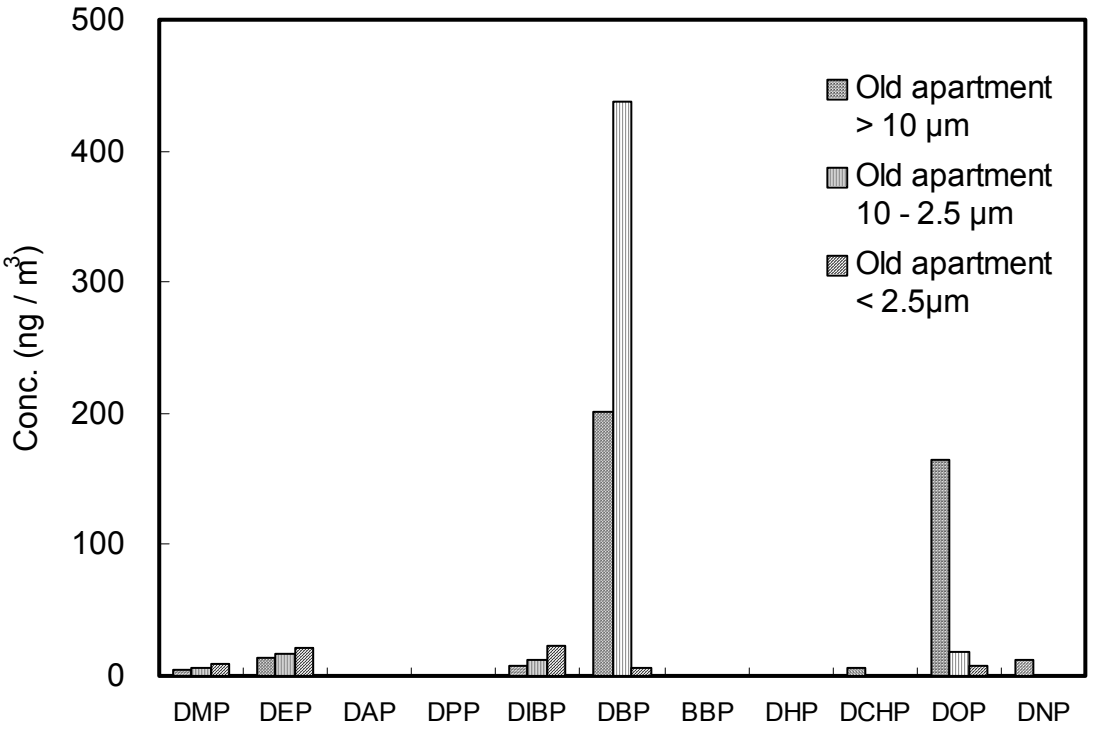

Figure 2. Example of measurement result of particle size distribution of phthalate esters in indoor air Sampling: 3L / min x 7 days

CONCLUSION

Obtaining accurate values in actual analysis of the P.E. in the air is difficult due to the presence of contaminating factors including the filter trapping the sample, the analysis operation itself, and environment in which analysis is done. In the research, the basic examinations such as reduction of the blank of the filters and recovery and examination of the contaminating factors were made. As a result, the following findings were obtained.

(1) For the filter trapping particulates, the glass fiber and quartz fiber filters thermally treated at 250 ºC tended to be low in blank. On the other hand, for the filter to be used for trapping gas, it was found that the commercial Carbon Disk Filter (untreated filter) packed in an aluminum bag was comparatively low in blank and that the blank was further reduced by cleaning with dichloromethane or the mixture solvent.

(2) A recovery test was made adding the standard P.E. solutions of 11 substances to the quartz and glass fiber filters and the Carbon Disk Filter. As a result, the recovery of more than 90 % was obtained when the mixture solvent was used.

(3) The P.E. are present in the indoor environment in large quantities. Accordingly, various types of contamination are conceivable during the experiment(sample taking, transfer, analysis). In the research, contamination of glass instrument by the oil on the hands and by the air in the room were simulated for experiment. As a result, it was found that P.E. were always present, adhering to the palm or fingers and that contamination took place when trapping filters were handled with contaminated hands. On the other hand, it was found that the concentration by P.E. was reduced by more than 80% by washing the hands with soap and warm water. On the hand, the contamination of the glass instrument from the air in the room was conspicuous, and it was found that storage of the glass instrument by wrapping with aluminum foil prevent contamination.

(4) This method was applied to the actual measurement of P.E. in the air in a room. As a result, it determined that they were always present both as particulates and gas. Especially, DBP and DOP concentration with a much output showed the high tendency. It was also found that in the particle size distribution, the concentration of fine particles not more than 2.5 μm tended to be high.

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