

# Quantitative Determination and Confirmation of Identity of Trace Amounts of Dialkyl Phthalates in Environmental Samples

by Gordon H. Thomas\*

## Introduction

Alkyl phthalates are used in industry for a wide variety of purposes such as plasticizers, lubricants, and synthetic intermediates. Their use as plasticizers for various types of synthetic resins and plastics is by far their most important industrial use.

Recently they have been receiving publicity as possible environmental contaminants, since such plasticizers can volatilize on incineration or be leached from plastics present in landfill projects. Evidence of their presence in soil organic matter (1,2) in water (3), and in fish (4) has been reported. Other reports pertain to their extraction from plastic tubing and from pharmaceutical containers used for storage (5,6). The isolation, identification, and specific localization of di-2-ethylhexyl phthalate in bovine heart muscle mitochondria has been reported (7). Furthermore, cause for concern has arisen with regard to their reported teratogenic effect in chick embryos (8) and rat fetuses (9).

Reports have recently focused attention on the need for confirmation of chemical identity in ultramicroanalysis, particularly with compounds isolated from environmental samples (10,11). The advent of combined gas chromatography-mass spectrometry (GC-MS) has assisted greatly in this problem of confirmation of chemical identity at submicro levels (12).

During the course of studies relating to confirmation of identity of polychlorobiphenyls (PCBs) in air samples by GC-MS, some unidentified peaks present in the gas chromatography-electron capture detector (GC-EC) profiles were characterized as phthalate esters. These findings prompted a more detailed study of dialkyl phthalates the results of which are presented in this paper.

Several examples are given in the literature for the separation of dialkyl phthalates by GC analysis. Both polar and nonpolar columns at low loading were used in conjunction with flame ionization or thermal conductivity detectors (13,14). The qualitative detection of low concentrations of dialkyl phthalates by using an electron-capture detector is documented (15), and the quantitative determination of trace amounts by use of this type of detector is also reported (16).

\* Ontario Research Foundation, Pesticide and Trace Analytical Laboratory, Sheridan Park, Ontario, Canada.

## Experimental

All reagents and apparatus were pre-extracted with hexane and/or acetone:benzene (19:1) until on examination by GC-EC, the resulting chromatographic profile of the extract was free from contaminating components.

A standard solution was prepared by weighing known amounts of di-ethyl, di-*n*-butyl, di-*n*-propyl, di-2-ethylhexyl, and dinonyl phthalate, and butylphthalyl butyl glycolate, transferring them to a 100-ml volumetric flask, and making up to the mark with hexane. Appropriate aliquots were taken for dilution in order to prepare a series of standard solutions of varying concentration. These solutions were chromatographed, and a plot of peak area versus concentration over the range 100-1000 ng was found to be linear for all components. The lowest limit of detection for butylphthalyl butyl glycolate was determined at 1.0 ng, while for the dialkyl phthalates the level was 10 ng.

### Sample Collection

An electrically operated pump was used to draw air through ethylene glycol contained in three traps connected in series. A filter was placed between the air inlet and the first trap to collect particulate matter from the air. Air was drawn through the filter and into the trapping solvent at a rate of approximately 1.7 ft<sup>3</sup>/min.

At the time of reporting, samples had been collected and analyzed from only one site, which is an air sampling station at the water works of the Municipality of the City of Hamilton, Ontario, Canada. The sampling station was made available for our use by the Air Management Branch of the Ontario Ministry of the Environment.

### Sample Analysis

Examination of a hexane extract of the filter by GC-EC did not indicate the presence of any phthalate esters.

The combined ethylene glycol from the three traps was shaken with hexane (50 ml x 3) for 30-min periods in a stoppered flask by using a wrist action shaker run at maximum agitation. The hexane was separated from the ethylene glycol, concentrated to dryness under reduced pressure at room temperature, and made up to a prescribed volume with hexane.

To show that the collection apparatus was an efficient trap for the phthalate esters entering it, several tests were made by adding known amounts of phthalate esters to trap #1, followed by drawing a known volume of air through the system. The ethylene glycol was extracted as above with hexane and the quantities of phthalates present in the extract determined by GC-EC. Recoveries of all phthalates was better than 90%.

### Liquid-Solid Chromatography

With the use of a plug of glass wool as a support, exactly 25 cm of Florisil was measured into a glass column (1 cm id) and topped with 2 cm of sodium sulfate. The hexane extract was transferred onto the column and washed in with a little hexane. By use of a graduated cylinder, enough hexane was added to bring the solvent volume to 80 ml, which was allowed to run through the column. When the hexane had reached the sodium sulfate, the receiver was replaced with another, and the column next eluted with a mixture of 25% ether/75% hexane (total volume of 80 ml). When the eluate reached the sodium sulfate the receiver was again replaced by another, and the column finally eluted with diethyl ether (200 ml).

The final ether eluate will contain any phthalate esters present in the original hexane extract, together with other highly polar components. Spiking experiments were performed for various concentrations of phthalate esters obtained after appropriate dilutions of the standard stock solution. Within the limits of experimental error, 100% recovery of the phthalate esters was obtained.

## Gas Chromatography

Gas chromatographic (GC) separations were carried out with a Varian Model 1200 instrument equipped with an electron-capture detector. The GC parameters used were as follows: column, 6 ft x 1/4 in., all glass; column packing, 3% SE30(Ultraphase) on Chromosorb W (AW-DMCS, 60/80 mesh); column temperature, 210°C; injector temperature, 230°C; detector temperature, 225°C; flow rate, N<sub>2</sub>, 25 ml/min.

## Gas Chromatography - Mass Spectrometry (GC-MS)

The MS used was an AEI MS-30 instrument with an electron bombardment ion source. The chromatograph used in conjunction with the MS was a Pye 104 series instrument. The interface between the GC and the MS was of all-glass design utilizing a single-stage silicone molecular membrane. The electron trap current was set at 400  $\mu$ A and the source temperature maintained at 230°C. The electron bombardment energy was set at 24 eV, slightly below the ionization potential of the helium carrier gas, so that small changes in helium pressure would not effect the total ion current. A total ion current monitor (TIC) is situated between the ion source and the mass analyzing magnet. This detector intercepts a portion of the ion beam and displays it as a voltage signal on a potentiometric strip chart recorder. When a chromatographic maximum is observed on the TIC recorder, the magnetic field is scanned (10 or 30 sec/decade), and the resulting mass spectrum is displayed on a three-channel oscillographic recorder.

The GC parameters used in conjunction with the MS were as follows: column, 6 ft. x 1/4 in., all-glass; column packing, 3% SE30 (Ultraphase) on Chromosorb W (AW, DMCS, 60/80 mesh); column temperature, 210°C; injector temperature, 230°C; interface temperature, 195°C; flow rate, He, 40 ml/min.

Sample preparation for GC-MS usually involved concentration of the hexane extract and take-up in a minimum of solvent, (depending on concentration of esters deter-

mined by GC-EC), followed by injection of a suitable aliquot.

## Results and Discussion

In Figure 1 a GC-EC profile of the standard mixture of dialkyl phthalates and the phthalyl glycolate is shown. The concentrations of the various phthalates in the solution used to produce this profile ranged from 15 ng of butylphthalyl butyl glycolate to 150 ng of each of the dialkyl phthalates.

Because of the decrease in sensitivity of the detector during prolonged running it is impracticable to construct a calibration curve for the estimation of phthalate esters present in environmental samples. To overcome this difficulty it is essential to inject a standard mixture after every few samples and to average the standard peak areas for

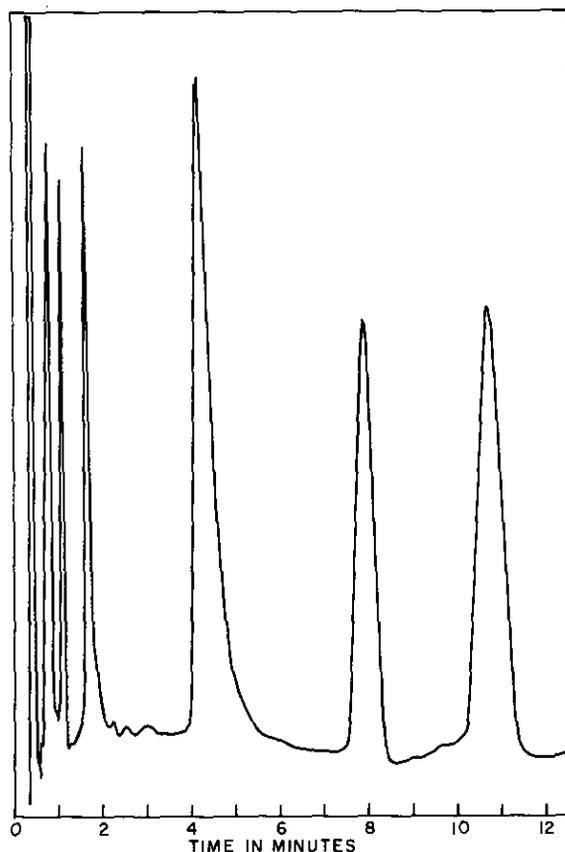


FIGURE 1. GC-EC profile of standard phthalate esters on SE 30 column.

calculating the concentration of esters present in sample extracts. If required, a better separation of the lower boiling dialkyl phthalates can be obtained by operating at a lower column temperature.

Figure 2 is included to illustrate a typical example of the type of GC-EC chromatographic profile obtained from an actual sample extract after Florisil chromatography. Figure 3 shows a corresponding GC-TIC chromatographic profile of the same extract.

Mass spectra were obtained on the peaks designated by a letter, and positive identification of the component present in the peak was accomplished. The components represented by the various peaks were characterized as di-*n*-butyl phthalate (A), butyl-phthalyl butyl glycolate (B), and di-2-ethyl-hexyl phthalate (C).

The mass spectrum of di-*n*-butyl phthalate is shown in Figure 4 as represent-

ative of the type of data obtained. A mass spectrum is usually presented as a bar graph obtained from an actual recorded spectrum by measuring peak heights and normalizing in terms of the most intense peak.

The electron impact mass spectra of dialkyl phthalates have been extensively studied by many workers (17-19). All spectra were relatively simple with few abundant ions, and the molecular ion intensities were shown to decrease rapidly with increasing size of the alkyl group. By far the most intense ion in the mass spectra of all dialkyl phthalates other than dimethyl phthalate was the one of  $m/e$  149 which is assumed to be a protonated anhydride even-electron ion. A peak due to an ion corresponding to loss of one alkyl group with two hydrogen atoms rearranged back to the carboxylic group on which the leaving group was originally attached to produce a protonated carboxylic

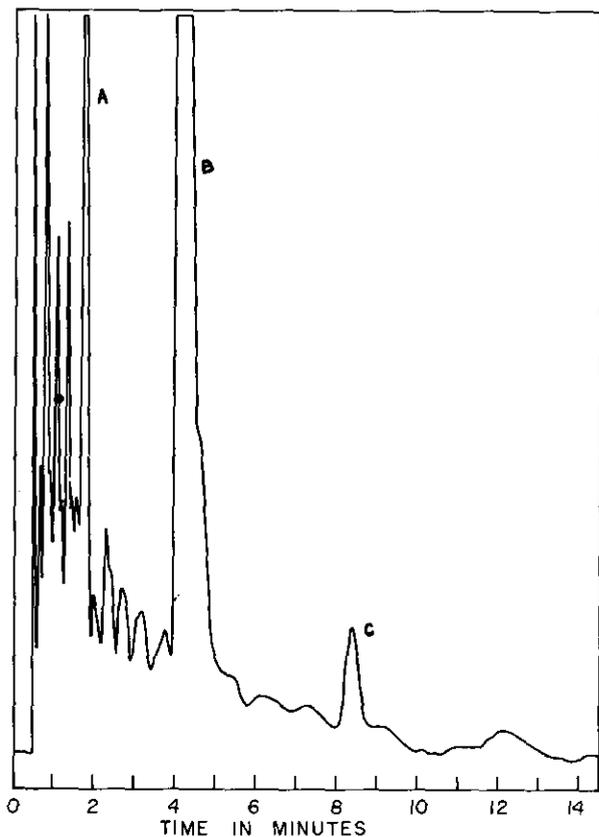


FIGURE 2. GC-EC profile of air sample extract after Florisil treatment.

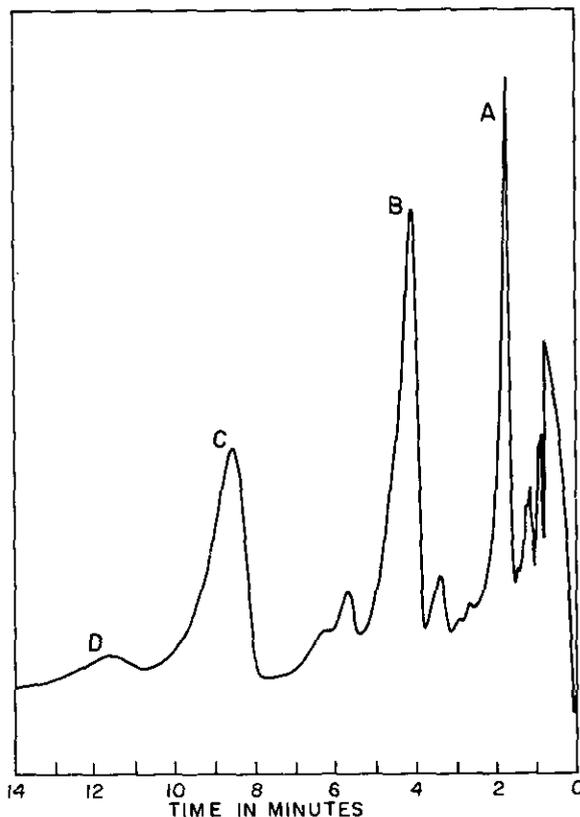


FIGURE 3. GC-TIC profile of air sample extract after Florisil treatment.

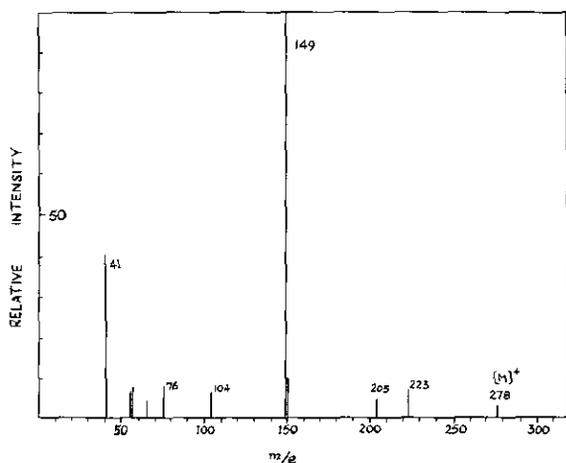


FIGURE 4. Mass spectrum of di-*n*-butyl phthalate.

acid ion was also observed. An ion peak which would be formed by the usual alkoxy radical loss typical of esters was also often present in the spectra. Mechanistically several paths leading to ion  $m/e$  149 species have been proposed, and it is quite likely that more than one route is operative.

Qualitatively the spectra obtained in this study follow the major paths outlined by these earlier workers. The spectrum obtained from the GC peak designated di-*n*-butyl phthalate had  $m/e$  149 as the base peak with peaks at  $m/e$  223 and  $m/e$  205, both with a relative abundance of 5%. A molecular ion was present at  $m/e$  278 plus a peak of small relative abundance at  $m/e$  167. That spectrum from the GC peak designated butylphthalyl butyl glycolate had  $m/e$  149 as the base peak with a major peak at  $m/e$  263 with a relative abundance of 41%. The spectrum from the GC peak designated di-2-ethylhexyl phthalate had  $m/e$  149 as the base peak, accompanied by others at  $m/e$  167 and at  $m/e$  279 of relative abundance 23% and 10%, respectively.

After positive identification by GC-MS, the concentrations of the respective components present in the air sample extract were determined by GC-EC. The results are recorded in Table 1.

It must be emphasized that the sampling site chosen for this experiment was adjacent to a municipal incinerator. The reason for the choice of this site was that the experi-

Table 1. Phthalate levels found in air samples.

Component	Phthalate levels (Site Municipality of city of Hamilton, Ontario, Canada, Water Works), ng/m <sup>3</sup>
Di- <i>n</i> -butyl phthalate	700
Butylphthalyl butyl glycolate	750
Di-2-ethylhexyl phthalate	300

ment being undertaken was initially for the collection and estimation of polychlorobiphenyls (PCBs), and it was assumed that high levels of these pollutants would be collected from such a site. The collection and detection of phthalate esters was incidental to that study, and consequently the data so far collected is scant. However, the levels indicated here are far higher than one would expect in ambient air, and this is undoubtedly a result of close proximity to an incinerator.

Since the first confirmation of identity of phthalate esters in GC-EC chromatographic profiles of air sample extracts, their presence has been detected and confirmed in paperboard and food packaging extracts.

The Ontario Research Foundation intends to carry out additional air monitoring experiments for phthalate esters utilizing widely different site locations.

### Acknowledgements

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