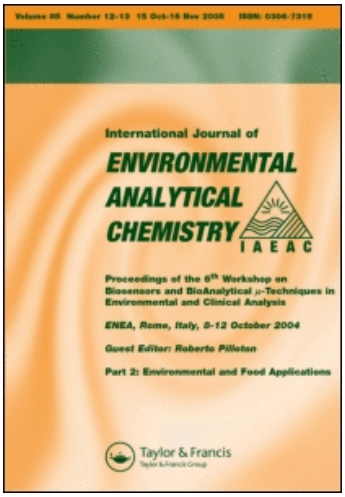

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A GC/MS Method of Determining Airborne DI-*n*-Butyl- and Di-(2-Ethyl Hexyl) Phthalates

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An analytical technique is presented that determines the amount of airborne phthalates in a glass fiber filter. The methodology makes use of a GC/MS system that has been integrated with a dedicated mini-computer.

KEY WORDS: Phthalate esters, air pollutants, GC/MS.

INTRODUCTION

Recently it was reported[1] that the United States Environmental Protection Agency (USEPA) has barred some companies from the manufacture of six new chemical compounds, claiming that these reagents interfere with human health and with the environment. The article continues to explain that this is the first time that the USEPA has used its authority under the Toxic Substances Control Act to prevent the manufacture of new chemical reagents that may be potentially dangerous to human health. While the article does not detail the specific compounds involved nor the chemical companies that were about to manufacture these reagents, the compounds are however identified as esters of phthalic acid that were to be used as plasticizers for polyvinyl chloride. It is further stated in this *Chemical and Engineering News* article that the USEPA prevented the manufacture of the compounds in question because the chemical firms had not provided the agency with human health effects

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data or information about the compounds' environmental fate. A spokesperson for the agency pointed out that there is evidence that related phthalate esters are already considered hazardous, and quoted a recently completed study performed by the National Cancer Institute that reported that mice and rats fed di(2-ethyl hexyl) phthalate developed liver tumors.

Earlier we reported[2] on 1975 ambient concentrations of di-(2-ethyl hexyl)-phthalate and di-butylphthalate at three New York City sampling stations (at Queens, Brooklyn, and Staten Island). Inasmuch as there will no doubt be greater interest in environmental phthalates, we should like to present a method for analyzing for airborne phthalates that makes use of GC/MS. The proposed technique makes use of the fact that the m/e 149 species is the most abundant ion in the mass spectra of a good many alkyl esters of phthalic acid. Certainly this is the case for both di-n-butyl- and di-(2-ethyl hexyl)phthalate.[3] Thus a calibration curve can be conveniently constructed plotting the 149/150 value against the micrograms of the corresponding alkyl phthalate. This methodology is described in the experimental section. Along with this analytical technique are presented some additional New York City ambient di-*n*-butyl- and di-(2-ethyl hexyl) phthalate values.

EXPERIMENTAL

A soiled Hi-volume glass fiber (8″ × 10″) was cut in half with clean scissors, placed into a loosely covered soxhlet extractor, and refluxed for 6 hours with 125–150 ml of benzene (Burdick Jackson). The top of the condenser was loosely covered during the extraction. The extract was then filtered through a fritted-glass Buchner funnel (ASTM 10–20), and the benzene removed using an all glass rotary evaporation. The funnel was rinsed with two 10-ml portions of Methanol (Burdick Jackson) and the washings combined. The residues were transferred to 10 ml vials using disposable pipettes with the aid of methylene chloride (Burdick Jackson). The solvent was then removed from the vial by passing a stream of filtered, dry nitrogen over the warmed solution.

Analyses were accomplished by adding a measured quantity of an internal standard and monitoring the relative intensity of the base peaks of the sample and the standard in a mass spectrometer. Data were recorded, stored and background automatically subtracted using a dedicated mini-computer data system.

Ring (4-deutero-) mono-deuterated isomers of di-*n*-butyl- and di-(2-ethyl hexyl) phthalates were selected for use as internal standards, since their chemical identity to phthalates being analyzed precluded selective transmission or decomposition in the Watson-Biemann Separator.

To each dry extract 100 microliters of a benzene solution containing 25 micrograms of 4-deutero-bis-(2-ethyl hexyl) phthalate and 5 micrograms of di-*n*-butyl phthalate (each containing 78% isotopic purity) were added. Approximately 1 microliter was injected into the gas chromatogrsph—the effluent being split between a flame ionization detector (F.I.D.) and the mass spectrometer. The peak height ratios were recorded for m/e 149 and m/e 150 after automatic background subtraction. The base peak ratios were converted to micrograms of di-(2-ethyl hexyl) phthalate using a calibration curve prepared by plotting intensity of (m/e 149)/(m/e 150) against the corresponding micrograms of di-(2-ethyl hexyl) phthalate and di-*n*-butyl phthalate. Figures 1 and 2 are the calibration curves for di-*n*-butyl- and di-(2-ethyl hexyl) phthalates respectively.

The following instrumentation conditions were used for calibration and analysis:

Gas Chromatograph	*Mass Spectrometer*	*Data System*
Perkin Elmer 800	*Nuclide 1270G*	*Incos 2100*
Column: Dexsil 300 (6%) on Chromsorb W Hap, (12 feet)	*Source Temp:* 225°C	Magnetic scanning, automatic background, subtraction parameter, set near minimum.
	Ionization Voltage: 70eV	
	Source Pressure: 2×10^{-6} torr	
Carrier Gas: Helium 40/ml/min.		
Column Temp: 255°C		
Injector Temp: 275°C		
Interface: Watson-Biemann (250°–300°C.)		

RESULTS AND DISCUSSION

High-volume samples were processed and analyzed for the presence and amount of di-*n*-butyl- and di-(2-ethyl hexyl) phthalates at six New York City sampling stations. These data are summarized in Table I, and lists the weight of total particulate matter (TSPM), the benzene extractables (B.E.) and the two phthalate esters.

No conclusion should be drawn from the data, inasmuch too few are presented. They should be viewed simply as examples of the analytical technique presented.

The GC/MS procedure for the quantitative determination of di-*n*-butyl- and di-(2-ethyl hexyl) phthalate is a convenient and rapid method for those laboratories that are equipped with GC/MS and the associated mini-computer data system. While the technique was tested on two esters, this writer sees no reason why the technique cannot be conveniently used for other phthalate esters.

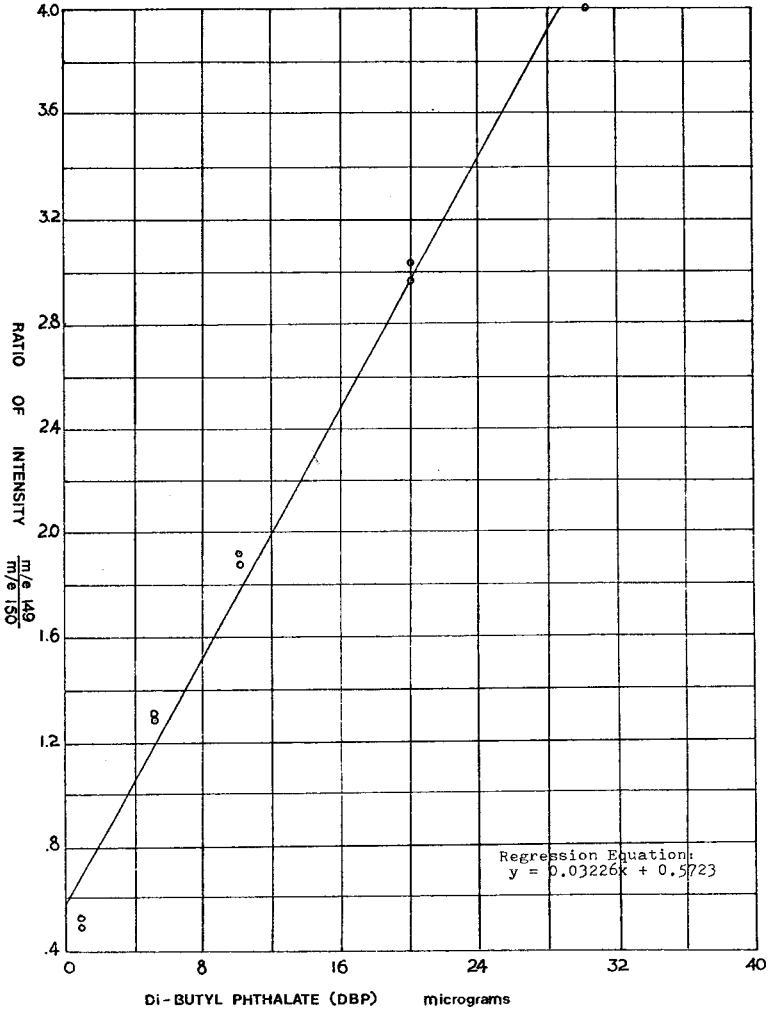

FIGURE 1 Calibration curve for di-*n*-butyl phthalate.

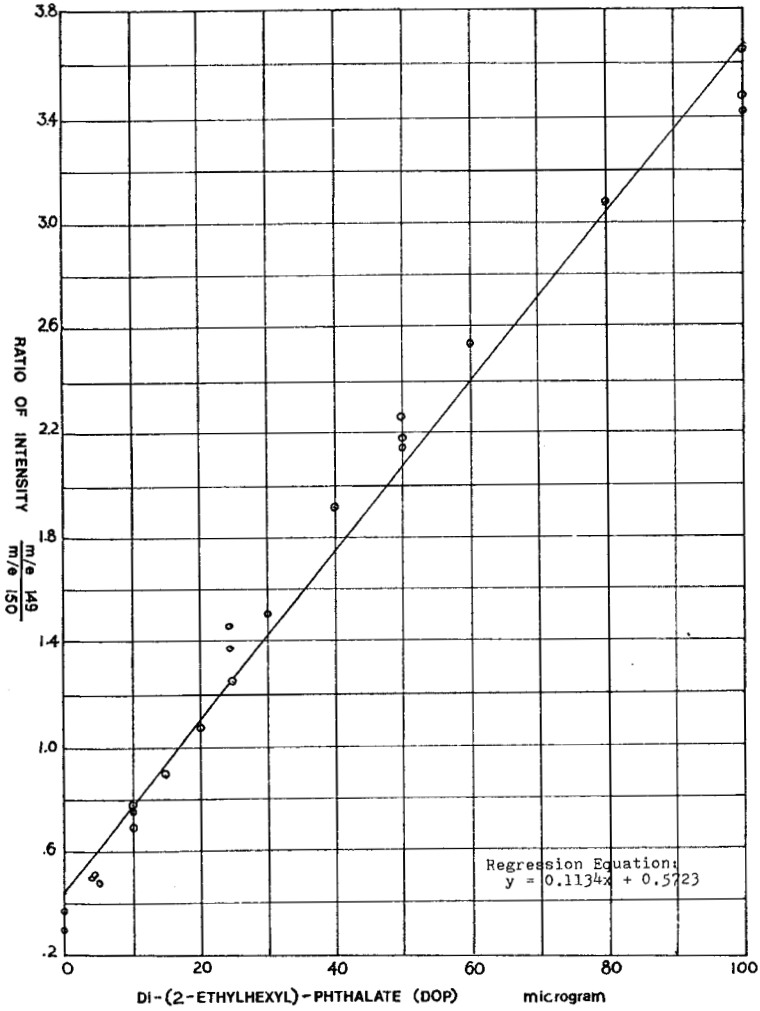

FIGURE 2 Calibration curve for di-(2-ethyl hexyl) phthalate.

TABLE I
Di-*n*-butyl and di-(2-ethyl hexyl) phthalate in N.Y.C. Dar Air Sampling Stations

Air-sampling Station Number	Date: August '75 (Day of the month)	Total Particulate Matter (TPM) (mg)	Benzene (a) extractables BE(mg)	%TPM	Phthalate (b) Dibutyl Di-(2-ethyl hexyl (micrograms) (DBP)	(DEHP)	TPM per DEHP $\times 10^{-3}$	μg DEHP per mg BE
3[c] Morrisania Health Center 1309 Fulton Ave. The Bronx	4	176	8.2	4.7	4	48	3.67	5.9
	10	200	11.0	5.5	4	48	4.17	4.4
6[c] Samuel Gompers High School 455 Southern Blvd. The Bronx	4	83	11.0	13.3	6	76	1.09	6.9
	5	91	9.0	9.9	8	58	1.57	6.4
	6	68	7.0	10.3	4	98	0.69	14.0
	8	94	8.4	8.9	6	58	1.62	6.9
	10	189	10.0	5.3	4	30	6.30	3.0
	11	211	10.8	5.1	4	104	2.03	9.6
	12	141	10.2	7.2	6	750	0.19	73.5
	14	99	7.0	7.1	8	54	1.83	7.7
10[c] Court House, City Hall Chambers Street Manhattan	10	189	24.0	12.7	8	30	6.30	1.3

26[d] Sheepshead Bay	4	237	7.6	3.2	0	4	59.25	0.5
High School	6	92	6.8	7.4	8	64	1.44	9.4
3000 Avenue X								
Brooklyn	11	233	13.0	5.6	6	54	4.31	4.2
30[d]	4	165	7.2	4.4	2	26	6.35	3.6
Springfield Gardens								
High School	10	185	8.6	4.6	4	14	13.21	1.6
Springfield Blvd &								
144 Ave., Queens								
31[d]	4	211	13.6	6.4	4	70	3.01	5.1
Goethals Bridge								
Plaza	10	157	6.0	3.8	0	14	11.21	2.3
Staten Island								
	4	237	7.6	3.2	4	26	9.12	3.4
	10	196	6.6	3.4	8	20	9.08	3.0

[a]Total weights reported were obtained by doubling the value found for the 4″ × 10″ weight.

[b]The background values for both dibutyl- and di-(2-ethyl hexyl) phthaltate were subtracted from their respective reported valued. (Note: Background values DBP = 4 micrograms/filter and DEHP = 8 micrograms/filter.)

[c]Samples collected at approximately 65 feet.

[d]Samples collected at approximately 40 feet.

Acknowledgements

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References

1. *Chemical and Engineering News*, **May 5,** 5 (1980).
2. Bove, J. L. and Dalven, P., *Intern. J. Environ. Anal. Chem.* **5,** 189–194 (1978).
3. S. Safe and O. Hutzinger, *Mass Spectrometry of Pesticides and Pollutants*, CRC Press, Cleveland, Ohio, p. 88, (1973.