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Gas Chromatographic Determination of *o*-Phthalic Acid Esters in Source Emissions

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The method of *o*-phthalate acid esters determination in effluent gases is described. Phthalates are adsorbed on a bed of Amberlite XAD-2. Desorption with acetone yields 100% recovery. Sample preparation for chromatographic analysis may involve separation from interfering hydrocarbons with the use of solvent elution from silica gel. Limit of determination for the individual phthalate is 0.1 mg m^{-3} for 30 l of air drawn through the adsorbing trap.

Praca zawiera opis metody oznaczaniu estrów, pochodnych kwasu *o*-ftalowego, w gazach odlotowych z instalacji przemysłowych. Ftalany są pochłaniane w rurkach wypełnionych amberlitem XAD-2. Desorpcja acetonem biegnie bez strat. Przed analizą chromatograficzną może być celowe oddzielenie frakcji ftalanów od węglowodorów przeszkadzających w analizie przez wybiórcze wymywanie rozpuszczalnikami z żelu krzemionkowego. Próg oznaczalności każdego z oznaczanych ftalanów wynosi 0,1 mg m^{-3} w 30-litrowej próbce powietrza.

Esters of *o*-phthalic acid are ubiquitous in the environment as a result of widespread use in chemical industry as intermediates in chemical syntheses, plasticisers, insect repellents and in cosmetic preparations. Total annual production has been estimated as 2×10^{10} kg [1]. Although human exposure from a variety of sources is likely, phthalates exhibit a low order of toxicity and owing to very low vapour pressure they pose minimal inhalation hazard as inhalation of significant amounts can occur only by spray or mist exposure. The U.S. threshold limit value for the occupational exposure for dibutyl phthalate, which is the commonest of all the

phthalates, is fixed at 5 mg m^{-3} time weighted average, as industrial experience indicates no reports of irritation or systemic effects in humans at this level [2]. The U.S. no observed adverse level for dibutyl phthalate is 3.8 ppb 24 hrs time weighted average for the ingestion route of exposure, while the ambient water quality criterion is 34 mg l^{-1} [3]. Phthalate input into the soil and potential uptake into crop plants may be of some concern as hepatotoxic [4], mutagenic [5] and carcinogenic [6] effects have been reported. However, in Poland there are no health safety standards referring to phthalates in atmospheric air explicitly.

Since phthalates are not volatile, appreciable concentration can be attained only in flue gases emitted at high temperatures. Spraying of liquid phthalates or adsorption on airborne particles should also be taken into account. To our knowledge no literature data on phthalate determination in source emissions are available. Procedures of environmental sampling and analysis are well developed, however. Bubblers filled with liquid absorbent such as ethylene glycol [7] or ethyl alcohol [8] seem to be less convenient than tubes filled with a solid sorbent and glass wool to filter out particulate matter. At higher flow rates activated charcoal is less efficient than Florisil [8,9] or Amberlite XAD-2 [10] which are especially suitable to adsorb dimethyl and dibutyl phthalates; for higher molecular weight phthalates polyurethane foam is recommended. Collection is followed by solvent extraction. The use of a variety of solvents has been described: 10% isopropyl alcohol in *n*-hexane [10]; acetonitrile followed by 20% petroleum ether in methylene chloride; or petroleum ether followed by diethyl ether or by isooctane [11]. Phthalates adsorbed on particulate matter can be isolated using glass fibers [12]. In this work we advocate the use of Amberlite XAD-2 which is a copolymer of styrene and divinylbenzene. Such a synthetic resin is only weakly polar and sampling of streams of high relative humidity presents no difficulties.

A few analytical techniques are available for phthalate determination. Ultraviolet absorption spectroscopy uses strong maxima at 210 and 220 nm as well as the weaker one at 260 nm. This method was developed for analysis of workroom air, but it suffers from the lack of selectivity [13,14]. Capillary gas chromatography is much superior in this respect. The columns have to withstand temperatures as high as 300°C. Methylpolysiloxanes, either pure or modified with phenyl or cyanide groups, are offered by many vendors. Three different detectors can be used. An electron capture detector is the method of choice at very low concentrations of phthalates in atmosheric air [7,9,10,15]. High purity nitrogen or 10% methane in argon can be used as auxiliary gases making it possible to achieve detection level as low as 0.01 ng. This detector is selective and initial purification of samples from hydrocarbons and other low electron affinity compounds can be avoided. The range of linear response is very narrow, however, and sensitivity to even traces of contaminants such as polycyclic aromatic hydrocarbons and halogenated compounds makes routine exploitation of the detector very cumbersome. A flame ionization detector is rugged and reliable but less sensitive. Its detection level amounts to 0.1–1.0 ng. The phthalate identity has to be established using mass detection as a supplementary technique. The use of quadrupole traps results in a detection level of 1.0 ng.

High performance liquid chromatography is also applicable. Acetonitrile in water is a mobile phase traveling through nonpolar C8 or C18 columns. UV detector operates at 220–280 nm.

Source testing considered in this work encompasses the material that is confined in a stack or duct. The limit of emission determination from a single source cannot be higher than 0.1–1 kg h^{-1}. Since a flow rate of gases may temporarily exceed 10000 m^3 h^{-1}, the limit of determination for the individual phthalate in the stream of gas should not be worse than 10–100 mg m^{-3}. Amberlite XAD-2 was selected as a sorbent on the basis of preliminary experiments and literature survey. Gas chromatography with flame ionization detection was chosen as an analytical method. The problems addressed in this work include selection of the most efficient solvent for desorption, establishment of the magnitude of extraction recovery coefficients and elaboration of gas chromatographic analytical conditions. Investigations are concerned with five phthalate esters: dimethyl phthalate (DMP); diethyl phthalate (DEP); di-*n*-butyl phthalate (DBP); *n*-butylbenzyl phthalate (BBP); and di-*n*-octyl phthalate (DOP). All these esters are included by the Environmental Protection Agency in a list of priority pollutants. The mixture of these particular phthalates is ordinarily used as plasticisers in plastics industry.

EXPERIMENTAL

Sampling and chromatography

AG-4U air aspirator equipped with a rotameter and mechanic flow controller was used as an air mover. The HP-5890 (Hewlett–Packard) and the GC-14A (Shimadzu) gas chromatographs, both equipped with flame ionization detectors, computer acquisition and processing systems and split/splitless injection port units for capillary columns were used. Mass spectrometric confirmation of peak identities was made using QP-5000 (Shimadzu) gas chromatograph/mass spectrometer with an access to mass spectra library. HPLC analyses were made with the use of SPD-M10A (Shimadzu) liquid chromatograph equipped with diode array detector.

Three capillary columns were employed: SPB-1, 15 m long, 0.53 mm ID, film thickness 1.5 μm; SPB-5, 30 m long, 0.25 mm ID, film thickness 0.5 μm, both obtained from Supelco; BPX-5, 25 m long, 0.32 mm ID, film thickness 0.25 μm, obtained from SGE.

Chemicals

Amberlite XAD-2, 20/60 mesh, manufactured by Alltech, was further purified by extraction with methylene chloride in a Soxhlet apparatus for 48 h. Every single extraction lasted about 15 min.

Silica gel, 0.2–0.5 mm, manufactured by Riedel–deHaën, underwent activation prior to use at a temperature of 250°C for 12–14 h, and was subsequently stored in a desiccator.

Millipore water was used. Analytical reagent grade acetone, methylene chloride, ethyl and methyl alcohol, manufactured by POCH Gliwice, were distilled with the use of six-step Vigreux column.

RESULTS AND DISCUSSION

Selection of extraction solvent

A number of solvents were tested to establish the magnitude of desorption coefficients. To a test tube filled with 250 mg of XAD-2, 10 μl of the mixture of five phthalates, 18–35 μg each, dissolved in methylene chloride was introduced with the

use of a microsyringe. The test tubes were stoppered, the contents mixed and let stand for 60 min. Extraction with 2 ml of individual solvent assisted with delicate shaking from time to time lasted about 5 min. The results listed in Table 1 indicate that acetone and methylene chloride show the best performance. On the basis of these results acetone was selected for further experiments as less toxic and more environment friendly than methylene chloride.

Table 1. Average desorption coefficients (%) for extraction of phthalates from XAD-2. Uncertainties shown in brackets are 1σ

	Desorption coefficients				
	Methanol	Ethanol	Acetone	Methylene chloride	*n*-Hexane
DMP	77.4 (7.3)	68.0 (2.6)	102 (4.1)	97.5 (6.3)	58.8 (3.1)
DEP	69.9 (5.0)	68.4 (2.3)	98.0 (5.6)	101 (6.7)	73.2 (3.9)
DBP	54.3 (3.9)	57.1 (7.0)	99.2 (4.8)	97.5 (5.8)	84.4 (2.9)
BBP	29.4 (4.3)	44.2 (1.3)	97.5 (4.4)	96.3 (6.9)	70.7 (0.3)
DOP	17.9 (2.4)	33.4 (1.3)	95.7 (8.2)	94.5 (9.9)	91.9 (0.3)

In subsequent experiments desorption efficiency was examined under conditions analogous to those used in sampling. Glass tubes were filled with two layers of XAD-2, 250 and 100 mg, respectively, separated and tightened on both sides with glass wool. Phthalate solution in methylene chloride, containing 90–180 mg of each phthalate, was sprinkled onto the front layer of glass wool using a microsyringe. 30–60 l of laboratory air was pumped through at flow rate of 60 l h^{-1}. Relative humidity of air was 80% at a temperature of 20°C. Desorption with 2 ml of acetone per every layer resulted in complete desorption. Recovery for all five phthalates has shown slight high bias lying over the range 103–106 ± 1.0–4.5%. Breakthrough of the first layer never happened. Exactly the same procedure was used to examine the effect of storage prolonged up to 7 days. Storing of samples for 1 day had no effect whatsoever on the recoveries. The decrease after 7 days storage was barely discernible, within the limits of experimental scatter.

Simulation of environmental sampling

Flue gases are frequently hot and may contain aerosol or particulate matter. Sampling should be carried out with sampling probes inserted in the duct at each of the points of flow measurement. The probe must be pointed directly upstream and the sampling rate adjusted to provide isokinetic conditions at each point. The experimental setup comprised an aspirator, a tube filled with two sections of XAD-2 sorbent, and a glass sampling probe, 0.7 m long, 0.5 cm ID. The heating wire is wound around the walls of the probe for temperature control and measurement. The sampling probe is connected with the tube with the use of teflon tubing, so that the outlet of the probe is in contact with the front tip of the tube. The final part of the tube, 10 cm, is not heated. The solution of phthalates administered at the front of the tube with a microsyringe undergoes partial or complete evaporation depending on the sampling probe temperature. 30 to 60 l of air is passed through this assembly at a flow rate of 60 l h^{-1}.

As considerable amount of phthalates is retained in the sampling probe even at higher temperatures, a procedure of washing the probe is necessary. Triplicate rinsing with 2 ml of acetone was found to be inadequate. A scroll of glass wool soaked with 0.5 ml of acetone was therefore applied to remove phthalates from the walls of the probe. Scrubbing with this scroll was accompanied by rinsing with acetone. The outlet of the probe was placed directly over the receptacle to discharge cleaning rinsings. After triplicate rinsing and cleaning the rinsings and glass wool were placed in a graduated bulb and sufficient acetone was added to make 10 ml. The results of gas chromatographic analysis are shown in Tables 2 and 3. The second section of XAD-2 has always been thoroughly tested for the presence of phthalates; breakthrough never happened, however. Thus, only data for phthalates in the first section are reported in the tables. To check the effects of high humidity, 30 l of the air containing water vapour mist sucked from above the water at a temperature of 90–100°C was passed through the sampling probe at a flow rate of 60 l h^{-1}. The cleaning procedure of the probe was the same as that described above. However, the tube with XAD-2 was dried by passing through it about 10–50 l of pure nitrogen.

Table 2. Average desorption coefficients (%) for extraction of phthalates from the sampling probe and the first section of XAD-2 (250 mg). Desorption with 2 ml of acetone; sample volume 30 l; mass of individual phthalates 18–35 μg. Probe temperature 24°C or 120–140°C (values in brackets)

	Desorption coefficients					
	Sampling probe		XAD-2		Total	
	24°C	120–140°C	24°C	120–140°C	24°C	120–140°C
DMP	40.8	[< 1]	29.5	[110]	70.4±5.0	[101±4.8]*
DEP	72.5	[< 1]	10.3	[98.1]	82.7±3.4	[98.1±14]
DBP	77.0	[< 5]	< 1	[60.6]	77.0±5.0	[60.6±5.3]
BBP	84.5	[21.3]	< 1	[50.5]	84.5±9.9	[71.9±8.1]
DOP	81.7	[36.1]	< 1	[53.1]	81.7±10.0	[89.2±6.9]

*Uncertainties are 1σ.

Table 3. Average desorption coefficients (%) for extraction of phthalates from the probe and the first section of XAD-2 (250 mg). Desorption with 2 ml of acetone; sample volume 30 l; mass of individual phthalates 90–175 μg. Probe temperature 120–140°C (values in brackets refer to experiments at enhanced humidity)

	Desorption coefficients					
	Probe		XAD-2		Total	
DMP	< 1	[< 1]	96.6	[90.3]	96.6±7.8	[90.3±4.5]*
DEP	< 1	[< 1]	101	[88.5]	101.0±8.6	[88.5±4.8]
DBP	12.4	[24.5]	92.0	[47.6]	104.4±12.7	[72.2±2.0]
BBP	55.0	[52.3]	45.0	[21.7]	100.0±8.0	[74.0±11]
DOP	67.2	[59.2]	22.0	[11.0]	89.2±6.9	[70.2±9.0]

*Uncertainties are 1σ.

Inspection of Tables 2 and 3 shows convincingly that cleaning of the sampling probe after every sampling is absolutely necessary. Temperature of the probe as well as the presence of water vapour are of little consequence. The higher the temperature, the smaller the amount of higher molecular weight phthalates remaining in the

sampling probe. However, even at a temperature as high as 200°C some phthalates persist deposited on the probe walls.

Recoveries are visibly smaller at lower phthalate concentrations. Apparently losses are due to adsorption on the walls. Recoveries improve if the amount of acetone used for rinsing is twice that used in the routine procedure, but this improvement is more than offset by increased dilution of the sample.

The summary results for recoveries of phthalates from either XAD-2 or XAD-2 preceded by the sampling probe are listed in Table 4. It is readily seen that use of the tube filled with XAD-2 yields 100% recovery for all practical purposes. Inclusion of the sampling probe results in a marked decrease in desorption coefficients. Large surface of the probe leads to enhanced adsorption. Also cleaning procedure involving as small as possible amounts of the solvent results in the loss of both recovery and accuracy of its determination.

Table 4. Average recoveries of phthalates from XAD-2 or XAD-2 and the sampling probe. Uncertainties are 1 σ

	XAD-2	XAD-2 plus probe
DMP	103 ± 1.3	90 ± 13
DEP	103 ± 3.4	93 ± 8.5
DBP	101 ± 2.7	70 ± 8.0
BBP	98 ± 3.8	83 ± 13
DOP	98 ± 3.8	83 ± 8.9

Chromatographic analyses

As diverse mixtures can be encountered in practice, different columns can be used. The SPB-1 column used in this work is a bonded nonpolar polymethyl siloxane polymer. The SPB-5 and BPX-5 columns are slightly polar since about 5% of the methyl groups have been substituted with phenyl groups.

A splitless mode of analysis has been used. A glass insert in the injection port was filled with small amounts of quartz wool. The temperature of the injection port was kept as a rule at 250°C; oven temperature was programmed over the range 100–300°C with increments amounting to 10–30°C.

Analytical conditions used in HPLC analyses were as follows: a Bakerbond PaH 16+ column, 25 cm×3 mm ID; mobile phase: acetonitrile plus water at a flow rate of 0.5 ml min^{-1}; gradient mode of operation was used: 0 to 4 min – acetonitrile/water 50/50; 4 to 40 min – linear enhancement in acetonitrile to 100%; 40 to 60 min – 100% acetonitrile. Diode array detector was employed over the 200–400 nm spectrum range; the best performance was found to be at 254 nm.

Determination thresholds for phthalates using different techniques: gas chromatography with FID, ECD and MS detectors and high performance liquid chromatography are given in Table 5 on the basis of the usual assumption that the peak can be determined if its height exceeds 5 times the peak-to-peak noise level. The data are only approximate, as the details of analytical conditions are disregarded. It is seen that sensitivity of GC/FID, GC/MS/TIC and HPLC/UV(254 nm) is similar, since GC methods can handle 1 μl samples while HPLC samples amount to 20 μl. The use GC/ECD and MS/SIM results in sensitivity enhanced by 1–2 orders of magnitude.

In the case of 30 l air sample, 2 ml of acetone is used for extraction and about 10 ml for probe cleaning. Given such conditions, any detector type is capable of achieving determination threshold below 0.05–0.1 mg m^{-3}. It leaves nothing to be desired as far as measurements of emissions are concerned.

Table 5. Determination thresholds for phthalates using different analytical techniques

	Determination threshold, ng			
	GC/FID	GC/ECD	GC/MS (TIC/SIM)*	HPLC/254 nm
DMP	0.2	0.02	0.5/0.05 (*m/z* = 163)	5.0
DEP	0.2	0.02	0.5/0.05 (*m/z* = 149)	5.0
DBP	0.2	0.02	0.5/0.05 (*m/z* = 149)	5.0
BBP	0.2	0.002	0.5/0.05 (*m/z* = 149)	5.0
DOP	0.2	0.02	0.5/0.05 (*m/z* = 149)	5.0

*TIC – total ion current; SIM – selected ion monitoring.

Interferences

Higher molecular weight aliphatic and aromatic hydrocarbons used as common solvents interfere with the determination of phthalates affecting the performance of electron capture and mass detectors, and making response of flame ionization detector inaccurate as a result of overlapping. Liquid chromatography offers a means to separate phthalates from interferences. Diesel oil was selected as a model material. It is a petroleum product consisting of C_8–C_{30} hydrocarbons with about 10-15% contribution from aromatics.

A column, about 15 cm×6 mm ID, extended to a funnel in the upper and contracted in the lower part, was filled with 1 g of silica gel and rinsed with 6 ml of *n*-hexane. Next 0.5 ml of the solution of phthalates, 0.18–0.36 mg ml^{-1}, and Diesel oil, 1.6 mg ml^{-1}, in *n*-hexane was introduced. The groups of alkanes and arenes could be separated from the phthalate fraction with the application of successive elutions using different solvents. First elution with 3 ml of *n*-hexane isolates alkanes; second elution with 3 ml of methylene chloride isolates aromatics; and, finally, elution with 3 ml of 50/50 solution of methylene chloride in methanol isolates phthalates. Separation was satisfactory as can be seen in Fig. 1. Recovery of phthalates was practically complete, amounting to 90–100%. A tenfold decrease in the initial phthalate concentration did not result in any deterioration of this performance.

Field experiments

Poly(vinyl chloride) manufacture facilities were investigated. Analysis of the material coming out of vents gave results shown in Table 6. Other phthalate esters as well as free *o*-phthalic acid itself were also determined and their presence confirmed by mass spectrometry. Representative chromatogram is shown in Fig. 2.

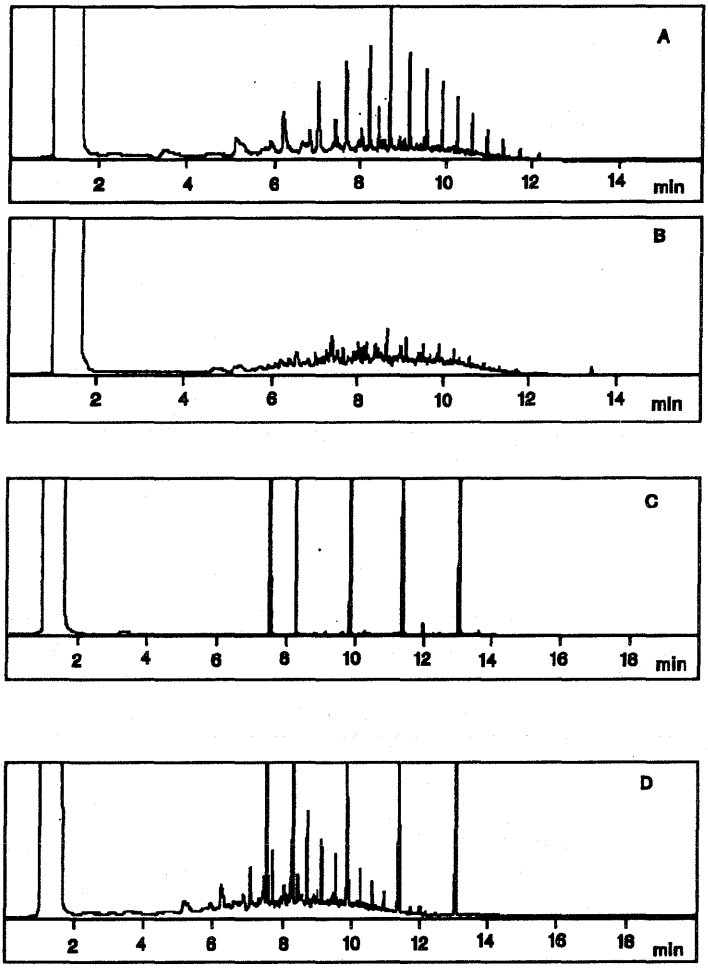

Figure 1. Chromatograms showing successive steps of purification procedure employing silica gel. A – aliphatic hydrocarbons; B – aromatic hydrocarbons; C – phthalates; D – sample prior to purification

Table 6. Field phthalate determination

		Concentration $g\ m^{-3}$	Emission $g\ h^{-1}$
Cold plasticising of PVC	DMP	< 0.001	< 1.0
	DEP	< 0.001	< 1.0
	DBP	0.01	27
	BBP	0.001	2.7
	DOP	< 0.001	< 1.0
Hot plasticising of PVC	DMP	< 0.001	< 1.0
	DEP	< 0.001	< 1.0
	DBP	0.016	47
	BBP	0.002	5.4
	DOP	< 0.001	< 1.0

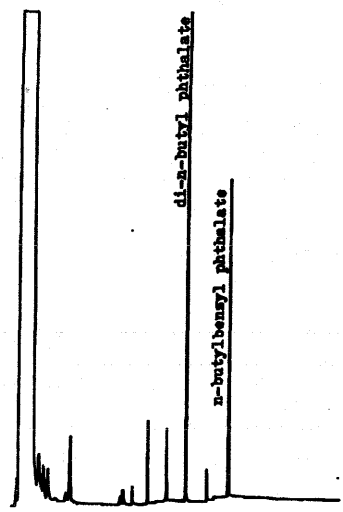

Figure 2. Chromatogram of the sample taken from gas released by vents of polyvinyl chloride manufacture facilities

Estimation of errors

Systematic and random errors contribute to the total error of quantitative analysis. The former ones can be estimated based on the known capacity tolerances of microsyringes, volumetric bulbs and pipets taking into account parallax effects. The latter errors refer to the determination of desorption coefficient and chromatographic analysis, and were estimated on the basis of standard deviation at the 95% confidence interval. The overall error of individual phthalate determination does not exceed 10%, if the sampling probe is not used, but increases to 15–20%, if it is.

Conclusion

For the preconcentration and storage of phthalate vapours from air streams Amberlite XAD-2 can be used as adsorbent. Solvent extraction with acetone, occurring with 100% efficiency, prepares the samples for chromatographic analysis. Sampling may involve the use of sampling probes; these have to be cleaned thoroughly after every sampling to avoid losses of analyte.

Determination threshold for the individual phthalate is about 0.1 mg m^{-3} from the 30 l effluent gas sample. Total accuracy of phthalate determination is 15–20 and 10% for the procedure with and without the use of probe for sampling. The method has been successfully tested under field conditions.

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