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Note

Rapid, sensitive, gas chromatographic determination of diethyl malonate and diethyl succinate in water facilitated by sorbent-tube pre-concentration

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Because dialkyl alkanedioates (esters of dibasic acids) are used as plasticizers in the coatings and plastics industry, their presence in the environment must be monitored. Several gas chromatographic (GC) methods have been published for the determination of these compounds[1–4], but most of these reports did not address the determination of these esters as trace contaminants in water. Junk *et al.*[4], however, reported an elegant procedure for such a determination involving adsorption of the ester on a XAD-2 column, elution with diethyl ether, dehydration of the eluate, evaporative concentration of the eluate and finally analysis by GC methods.

We report here a relatively simple, rapid determination of diethyl malonate (DEM) and diethyl succinate (DES) in water based on the vapor-phase pre-concentration of solvent extracts on solid sorbent pre-concentrator tubes and the subsequent thermal desorption of these tubes into a gas chromatograph. The concept of pre-concentrating solvent extracts in the vapor phase is not new; for example, it has been employed previously for determinations of hydrazine and related species in air[5], as well as for determinations of isopropyl methylphosphonofluoridate in water[6]. However, this principle is surprisingly little used in view of its relative simplicity, its general applicability and its potential for achieving simultaneously high levels of accuracy, precision and sensitivity. The particular method given here provides useful signals for either DEM or DES at levels corresponding to aqueous sample concentrations down to approximately 3 ng ml^{-1} when, in order to maximize the sensitivity of the method, the entire sample extract is pre-concentrated, or down to approximately 25 ng ml^{-1} when, in order to reduce the analysis time and the complexity of routine sample manipulations, only a small portion of the extract is pre-concentrated. The relative standard deviation of replicate determinations is typically less than 5% at analyte concentrations ten (or more) times higher than the working lower limit for quantitative determinations.

EXPERIMENTAL

Fabrication of solid sorbent pre-concentrator tubes

The solid sorbent pre-concentrator tubes were prepared and conditioned as described previously[6] except that 60–80-mesh Chromosorb 101 was employed as the

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sorbent material. Relative to 50–80-mesh Porapak Q and 60–80-mesh Tenax-GC, this sorbent yielded fewer extraneous chromatographic peaks in the vicinity of the analyte peaks upon its thermal desorption into the gas chromatograph. Each of these porous polymer sorbents was purchased from Supelco (Bellefonte, PA, U.S.A.).

Preparation of calibration standards

Standard solutions of DEM and DES for use in the calibration of the instrumental response were prepared in distilled, deionized water by conventional serial dilution of concentrated stock solutions. To avoid errors caused by hydrolysis of the esters, the stock solutions and calibration standards were prepared fresh daily. The solutions were stored in vials with PTFE-lined caps. The prepared standards typically covered the concentration range from about 25 to approximately 10,000 ng ml^{-1}, and the standards lying closest to the 'unknown' sample values were then employed for linear regression analysis in computing the 'unknown' analyte concentrations.

Extraction

A 2-ml aliquot of each aqueous sample and standard was extracted with 1.0 ml of reagent-grade diethyl ether by vigorously shaking a vial containing the two phases for 3 min. The ether layer was allowed to separate for at least 30 sec, and an aliquot of the ether that varied from 10 to 100 % of the available ether layer (usually about 10 %, *i.e.*, 100 μl) was withdrawn by syringe in preparation for the pre-concentration step.

Pre-concentration

A solid sorbent pre-concentrator tube was attached by means of PTFE tubing to the narrow end of a glass pipet dropper tube filled with silanized glass-wool. The opposite end of the pre-concentrator tube was then connected, also with PTFE tubing, to an air sampling pump. After the pump had been switched on and adjusted to sample at a rate of about 100 ml min^{-1} into the dropper tube, the aliquot of ether extract was deposited by syringe directly into the plug of glass-wool within the dropper tube. The ether solution immediately wet the glass-wool, resulting in a rapid rate of evaporation. The ether and analyte vapors were thereby swept into the sorbent bed, which trapped the analyte quantitatively while allowing most of the solvent vapor to pass through. Pumping was continued for approximately 10 min to effect the transfer of all analyte vapor to the sorbent bed. Experiments in which the gas exiting from the sorbent tube was analyzed for DEM and DES disclosed that no significant breakthrough of these substances occurred under these conditions even at the highest analyte concentrations encountered in this work (*i.e.*, about 10,000 ng ml^{-1} in water).

Desorption and analysis

A Model 5830A gas chromatograph (Hewlett-Packard, Palo Alto, CA, U.S.A.) equipped with a flame-ionization detector was employed for all determinations of DEM and DES. To permit the thermal desorption of pre-concentrator tubes directly on to the GC analytical column, the instrument's injection port was modified according to the method of Fowler *et al.* (method A)[7]. To desorb a pre-concentrator tube, therefore, the tube was simply inserted into the hot, modified injection port, and the carrier gas (nitrogen) flow was then rerouted through the tube to initiate the chromatographic process. The resulting chromatographic response was

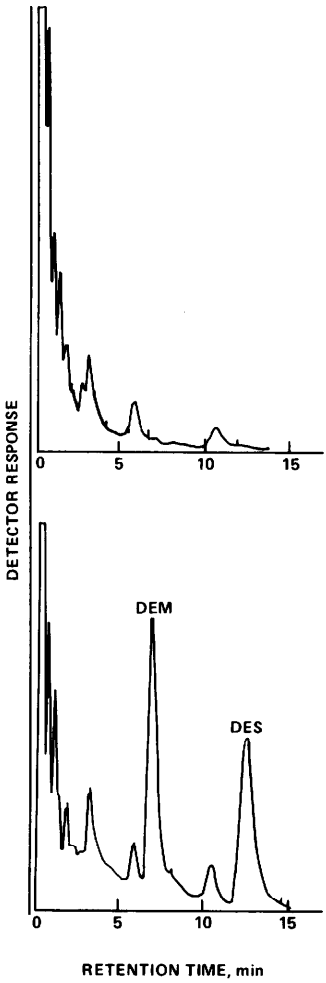

Fig. 1. Chromatograms obtained from desorption of pre-concentrator tubes. The upper panel shows the results obtained from the desorption of a pre-concentrator tube that had been treated with diethyl ether. The lower panel shows the results obtained from the desorption of a pre-concentrator tube that had been treated with a sample containing both DEM and DES. The amount of each compound on the column was 100 ng.

quantified either automatically by electronic integration of the peak area or else manually as the product of the measured peak height and the peak width at half-height.

The GC column consisted of a 180-cm length of 3.0 mm O.D., 1.5 mm I.D. PTFE tubing packed with 5% QF-1 and 3% DC-200 on 60–80-mesh Gas-Chrom Q. The modified injection port was operated at 195°C and the column oven at (or near) 100°C. The carrier gas flow-rate was maintained at 18 ml min^{-1}. Under these conditions, DEM and DES eluted at 7.4 and 13.2 min, respectively (see Fig. 1).

RESULTS AND DISCUSSION

During a typical calibration exercise involving the use of seven DEM standards, a linear least-squares fit of detector signal(s) *versus* concentration (c) for the seven standards yielded an equation $s = (4.50 \cdot 10^1 \pm 4.00 \cdot 10^{-1}\ \text{mm}^2\ \text{ml ng}^{-1})c + (1.33 \cdot 10^3 \pm 2.40 \cdot 10^3\ \text{mm}^2)$, with a standard error of the estimate ($S_{y.x}$) of $4.41 \cdot 10^3$ mm^2 for signals between $1.20 \cdot 10^3$ and $4.71 \cdot 10^5$ mm^2 and for concentrations between $2.60 \cdot 10^1$ and $1.06 \cdot 10^4$ ng ml^{-1}, and with a correlation coefficient (r) of 0.9998. These results were obtained with the use of 100-μl aliquots of the ether extracts and with the electronic peak integration method.

In a similar calibration of the instrumental response to DES, linear regression analysis of the data (seven standards) produced the equation $s = (3.09 \cdot 10^1 \pm 8.00 \cdot 10^{-1}\ \text{mm}^2\ \text{ml ng}^{-1})c + (6.55 \cdot 10^2 \pm 3.78 \cdot 10^3\ \text{mm}^2)$, with $S_{y.x} = 8.61 \cdot 10^3\ \text{mm}^2$ and $r = 0.9986$. The concentrations of the standards and the amplitudes of the measured signals were virtually the same as those given above for DEM.

In each of these calibration exercises, the signal obtained from the most dilute calibration standard was roughly of the same magnitude as the y-intercept, a result of the unusually large range of concentrations spanned by these data. Clearly, therefore, these regression equations would be of little use at the lower end of the calibration range. For work at the lower end of this range, only the lower calibration standards should be used, so that the y-intercept lies closer to zero. However, these data do indicate that the linearity of response is excellent over a broad range of concentrations and that the errors resulting from the use of these data are suitably small for most applications at the higher concentrations. Moreover, in ten separate measurements of an aqueous DEM standard whose DEM concentration was 1055 ng ml^{-1}, the relative standard deviation was 3.9%.

In the calibration experiment for DEM, the most dilute standard ($2.60 \cdot 10^1$ ng ml^{-1}) generated a chromatographic peak whose amplitude was approximately eight times the peak-to-peak noise amplitude at the baseline. Because the DEM peak was not completely resolved from a minor extraneous peak that invariably appeared as an artifact of the thermal desorption process, no measurements at concentrations below this level were attempted when only 100 μl of the ether extract were taken for analysis (the extraneous peak also featured a signal-to-noise ratio of about 8). However, the amplitude of this extraneous peak was largely independent of the volume of extract evaporated into the pre-concentrator tube, and therefore the sensitivity could be increased merely by increasing the volume of extract. When the entire extract was pre-concentrated, DEM signals produced by 3 ng ml^{-1} solutions of DEM were comparable to those of the extraneous peak. In any event, no formal determination of detection limit was attempted.

We concluded that the method described herein was effective for the determination of DEM and DES in water at concentrations down to the low parts per billion range. The method required about 20 min per sample after calibration of the instrument, although this sample turnover rate could have been improved considerably by the simultaneous use of, for example, more than one pre-concentrator sampling pump or an automatic sample shaker in the extraction step. The efficiency of the extraction was found to be essentially 100% for both analytes. In principle, this method should be useful for determinations of any suitably stable, moderately volatile organic substance with favorable water/ether partitioning characteristics.

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