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TRACE IMPURITIES IN SOLVENTS COMMONLY USED FOR GAS CHROMATOGRAPHIC ANALYSIS OF ENVIRONMENTAL SAMPLES

W. D. BOWERS and M. L. PARSONS*

Department of Chemistry, Arizona State University, Tempe, AZ 85281 (U.S.A.)

and

R. E. CLEMENT, G. A. EICEMAN* and F. W. KARASEK

Guelph-Waterloo Graduate Centre, Chemistry Department, University of Waterloo, Waterloo, Ontario N2L 3G1 (Canada)

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SUMMARY

Distilled-in-glass and pesticide grade solvents commonly used in analyses of environmental samples for organic compounds at trace concentration levels were condensed 2000 fold and analyzed by gas chromatography, gas chromatography–mass spectrometry and selected ion monitoring. Cyclohexane, methylene chloride and methanol solvents each contained an estimated total of 1–150 ng of organic impurities per ml of uncondensed solvent. Impurities identified by mass spectra included phthalate esters, *n*-hydrocarbons and chlorinated hydrocarbons; however no solvent contained all of these impurities. Pesticide grade solvents contained up to 21 components with maximum concentrations per single component of 30–50 ng/ml in the uncondensed solvent. Distilled-in-glass grade solvents had fewer and lesser amounts of similar impurities, and were found to be the most suitable for trace organic analysis.

INTRODUCTION

Analysis of environmental samples for organic compounds which are present at trace concentration levels frequently involves solvent extraction followed by condensation of the extract by factors of 200–2000. Since components in some samples may be present in microgram to picogram ranges, these large condensation factors are necessary to produce extracts of sufficiently high concentrations for analyses by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS)[1,2]. Introduction of artifacts into extracted samples from sources such as solvents, glassware and storage vials can produce significant contamination in the condensed extract and lead to erroneous conclusions regarding sample composition[3]. However, for reducing introduction of artifacts, the purity of solvents used for extracting organic

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* Present address: Department of Chemistry, New Mexico State University, Las Crusas, NM 88003, U.S.A.

material at trace concentration levels from environmental samples is crucial for un-ambiguous analytical results. Many trace analytical procedures currently in use employ cyclohexane, methylene chloride or methanol of high purity as the extracting solvent and different commercial grades including analytical reagent (AR)[4,5], pesticide (PG)[6,7] and distilled-in-glass[8-10] have been used. An exhaustive literature search indicated that there have been very few papers concerning trace impurities in organic solvents[11-16]. Of these papers, one[16] found an average concentration of 60 ppb for dibutyl and di-2-ethylhexyl phthalates in high purity solvents following a 200-fold concentration step.

In testing the usefulness of selected solvents for determination of organic compounds present at trace levels in environmental samples, different grades of cyclo-hexane, methylene chloride and methanol were obtained and analyzed for their organic content by GC and GC–MS following a 2000-fold condensation. We report here the concentration and identification of impurities detected in condensates of these solvents.

EXPERIMENTAL

Solvents

Pesticide grade methanol, cyclohexane and methylene chloride were obtained from Fisher Scientific (Fairlawn, NJ, U.S.A.). Distilled-in-glass grade methanol, cyclohexane and methylene chloride were obtained from Burdick & Jackson (Muske-gon, MI, U.S.A.) and Caladon Labs. (Georgetown, Canada).

Sample preparation

A 200-ml aliquot of each solvent was condensed by rotary evaporation under aspirator vacuum to approximately 10 ml in a 250-ml round-bottom flask. This con-densate was transferred with several rinsings of fresh solvent to a 25-ml pear-shaped flask where the condensate was further reduced in volume to about 300 μl by rotary evaporation. The sample was then transferred to a 1.0-ml reacti-vial (Pierce, Rock-ford, IL, U.S.A.) equipped with screw cap and PTFE liner. A gentle stream of high purity (99.995%) nitrogen gas was directed across the mouth of the sample vial to reduce the condensate to a final volume of 100 μl. Two to four replicate samples of each solvent were prepared and analyzed by GC and GC–MS including selected ion monitoring (SIM).

All glassware was washed with an aqueous solution of Alconox detergent (Alconox, Inc., New York, NY, U.S.A.) in an ultrasonic bath, thoroughly rinsed with deionized water, dried at 300°C for 1 h in a general purpose laboratory oven and used immediately upon cooling to ambient temperature.

GC analysis

All solvent condensates were analyzed using a Hewlett-Packard 5830A digital gas chromatograph equipped with a flame ionization detector (FID) and a glass column (3 m × 2 mm I.D.) containing Aue packing[17,18]. Operating conditions were: initial temperature, 80°C; program rate, 4°/min; final temperature, 250°C; injection port temperature, 250°C; FID, 300°C; helium carrier flow-rate, 35 ml/min; sample size, 3.0 μl; attenuation, 16; and slope sensitivity, 0.1 mV/min.

Before the analysis of each sample, column blanks were run to determine concentration levels of artifacts introduced by septum or column. For a column blank, the FID response was recorded during a complete, temperature-programmed analysis by GC with no introduction of sample or solvent.

GC–MS analysis

A Hewlett-Packard 5992 GC–MS–Calculator system was equipped with a glass column (1.9 m × 2 mm I.D.) containing Aue packing, a single flexible disc, X–Y plotter, silicone rubber membrane seperator and quadrupole mass analyzer. Conditions of analysis were: initial temperature, 90°C; temperature program rate, 4°/min; final temperature, 250°C; injection port temperature, 250°C; helium carrier flow-rate, 40 ml/min; and solvent time-out, 3 min. Several components detected by GC–FID were not detected by GC–MS because they were eluted during the solvent time-out period. Mass spectrometer operating conditions were optimized daily using AUTOTUNE software. Condensates were analyzed by GC–MS using the scanning mode and the more selective and sensitive SIM mode. A column blank and procedure blank were run prior to each analysis. The procedure blank consisted of an injection of the uncondensed solvent and analyzed under identical conditions as the condensed solvent. This monitors the artifacts introduced by the syringe, septum, column and other instrument sources. Chromatographic conditions were modified when necessary to resolve and assign identities to components which eluted near the solvent peak under conditions listed above. These modified conditions were: initial temperature, 30°C; initial time, 3 min; temperature program rate, 2°/min; final temperature, 250°C; and solvent time-out, 2 min.

In using SIM analysis, the ion fragments for the compounds or compound classes monitored were: 74.1, methyl esters; 85.1, n-hydrocarbons; 163.1, methyl phthalate; 149.1, other phthalate esters; 202.1, pyrene, fluoranthene; and 252.1, benzopyrenes.

GC and GC–MS analysis of standard solutions

A standard solution (GCCAL) containing n-hydrocarbons, phthalate esters, 1-alcohols and polycyclic aromatic hydrocarbons (PAH) in cyclohexane was used for determining FID response factors. An average response factor of 400 area counts per ng for organic compounds was used later for quantitation of integrated data from GC analysis.

The identification of n-hydrocarbons and phthalate esters in the condensates from SIM analyses was based on matching m/e values and retention times with values of known compounds in the GCCAL solution analyzed under identical SIM conditions. Components detected in analysis by scanning GC–MS were identified using mass spectra which were then compared to reference spectra[19,20]. For some spectra the NIH/EPA Chemical Information System (CIS)[21] including both the Mass Spectral Search System (MSSS) and the Probability Based Matching (PBM) was used as an aid in identification.

Computer analysis of data

Kováts' retention indices were calculated using the computer program RICALC and bar-graph plots were produced by the program GCPLOT using a Calcomp plotter.

Both programs were written in the FORTRAN IV language and have been described previously[22].

RESULTS AND DISCUSSION

Cyclohexane

 Results obtained from GC analyses of three different cyclohexane condensates are displayed in Fig. 1 as a GCPLOT. Full scale values (F.S.) which are listed in the upper right corner of each plot are rough indicators of concentration and have been normalized to 50,000 in all plots to facilitate visual comparisons. The estimated total concentrations of organic compounds in each cyclohexane sample were calculated using peak areas from GC–FID analyses of the condensates and are given in Table I. Estimated limit of detection for GC–FID in this study is 0.5 ng/ml of uncondensed
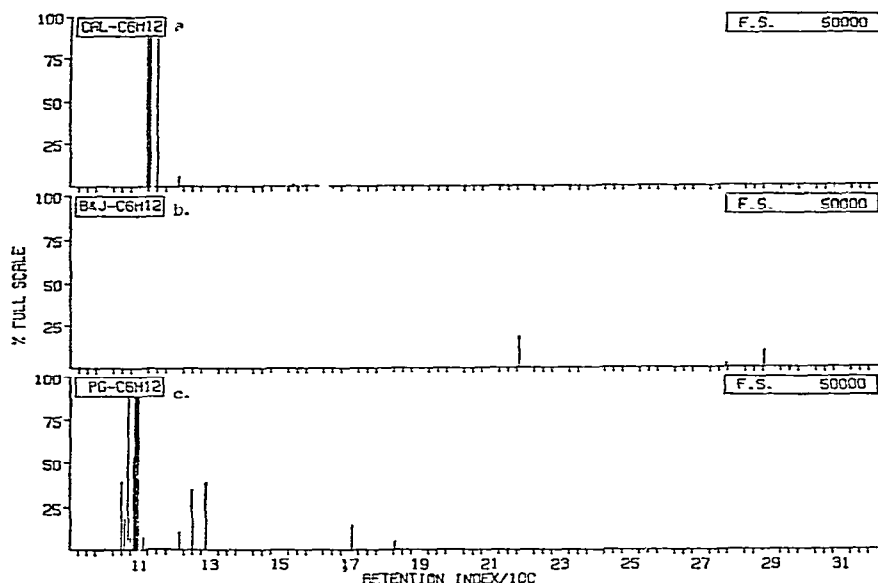

Fig. 1. GCPLOT of data from GC–FID analyses of cyclohexane condensates of CAL (a), BJ (b) and PG (c) solvents.

TABLE I

TOTAL ESTIMATED CONCENTRATIONS (ng/ml) OF ORGANIC COMPOUNDS IN UNCONDENSED SOLVENTS

GC–FID response factors for various types of organic compounds range from 226 to 456 area counts per nanogram. Area counts were converted to nanograms using an average response factor of 400 area counts per nanogram.

Solvent	*Manufacturer or grade*		
	CAL	BJ	PG
Cyclohexane	95	6.4	150
Methylene chloride	<1	17	100
Methanol	2.5	27	65

solvent while a component which is 100% F.S. in the GCPLOT is equal to 20 ng/ml of uncondensed solvent.

Several impurities consisting primarily of low-molecular-weight compounds which eluted between retention indices 1025 and 1175 in Fig. 1a and c were detected by GC–FID in the Caladon (CAL) and pesticide grade (PG) cyclohexane condensates, however, similar impurities were not detected (see Fig. 1b) in the Burdick & Jackson (BJ) condensate. Components with much lower concentrations and longer elution temperatures were found in each condensate, although small differences in the condensates were apparent in the number, concentrations and elution times of these components. Analysis of PG condensate by GC–MS showed five components at retention indices from 1200 to 1828 and at concentration levels of 0.9–29 ng/ml uncondensed solvent while fewer components at low concentration level (<1 ng/ml) were detected in each of the two distilled-in-glass grade solvents (BJ and CAL) between retention indices 1200 and 2900. Replicate samples of each solvent were analyzed by GC–FID and the percent reproducibility determined for peak areas and retention times based on the average values of selected components in each sample. Reproducibilities of retention times for these components were 1–5% relative standard deviation (RSD) while reproducibilities of peak areas were 1–95% RSD. Column blanks which were run before GC–FID analyses of each cyclohexane condensate were free of detectable impurities except for a few components of low relative concentration which consistently appeared in both column blank and sample chromatograms and were removed from the data before plotting.

Results from GC–MS analyses of cyclohexane condensates are given in Table II. Compounds which had retention indices below 1140 in Fig. 1a and 1b and 1080 in Fig. 1c eluted during the solvent time-out period, even using the modified conditions for GC–MS analysis. A major component of CAL condensate at retention index 1150 had a M^+ at 100 a.m.u. and is very similar to cyclohexanol, $C_6H_{12}O$. Two components detected by GC–FID in BJ condensate were detected by GC–MS and were identified as diethyl and dioctyl phthalates. In the PG condensate satisfactory mass spectra were obtained for components at retention indices of 1085, 1095, 1110, 1210, 1250, 1290, 1705 and 1828. Three components were identified as n-butyl n-butyrate (1085) and tributyl phosphate isomers (1705, 1828) while the remaining components were not identified.

Selected ion monitoring is often used in analysis of environmental samples where high sensitivity and selectivity are required and is illustrated in Fig. 2 which shows a plot of SIM data for three analyses including PG cyclohexane condensate and GCCAL solution using the m/e value 149.1. The retention times of known phthalate esters were matched with retention times of components for identification while integrated peak areas were used for quantitation of individual components. Data from SIM analysis of condensates for each compound or class of compounds were also compared to known compounds for identification and quantitation. Results from SIM analysis of cyclohexane condensates are presented in Table III. No PAHs with m/e values 202.1 and 252.1 or methyl esters, m/e 74.1, were detected in any cyclohexane condensate although each sample contained some phthalate esters and the BJ condensate contained n-hydrocarbons from $C_{24}H_{50}$ to $C_{30}H_{62}$. Column and procedure blanks were analyzed using SIM prior to SIM analyses of each sample and these results used in correction for instrumental artifacts.

TABLE II

IDENTITIES AND CONCENTRATIONS OF ORGANIC COMPOUNDS IN SOLVENTS BY GC-MS

RI values and concentrations based on GC-FID data; identities based on GC-MS.

Solvent	CAL			BJ			PG		
	RI	*Compound*	*ng/ml*	*RI*	*Compound*	*ng/ml*	*RI*	*Compound*	*ng/ml*
Cyclohexane	1150	$C_6H_{12}O$	49	2180	Diethyl phthalate	3.5	1085	n-Butyl n-butyrate	29
				2878	Dioctyl phthalate	1.8	1705	Tributyl phosphate isomer	2.9
							1828	Tributyl phosphate isomer	0.89
Methylene chloride	None			2200	Diethyl phthalate	0.52	1027	1,1,1-Trichloropropane	16
				2350	Dibutyl phthalate	7.7		1,2,3-Trichloropropane	
							1038	1,1,1,2-Tetrachloropropane	21
							1155	Tetrachloroethane	1.9
							1655	Phthalic anhydride	0.42
							2760	Dioctyl phthalate	14
Methanol	None			None			1265	C_9H_{12}; 1,4-Bis (methylene)-cyclohexane	1.6
							1475	$C_8H_{10}O$; 2,6-Dimethylphenol	2.6

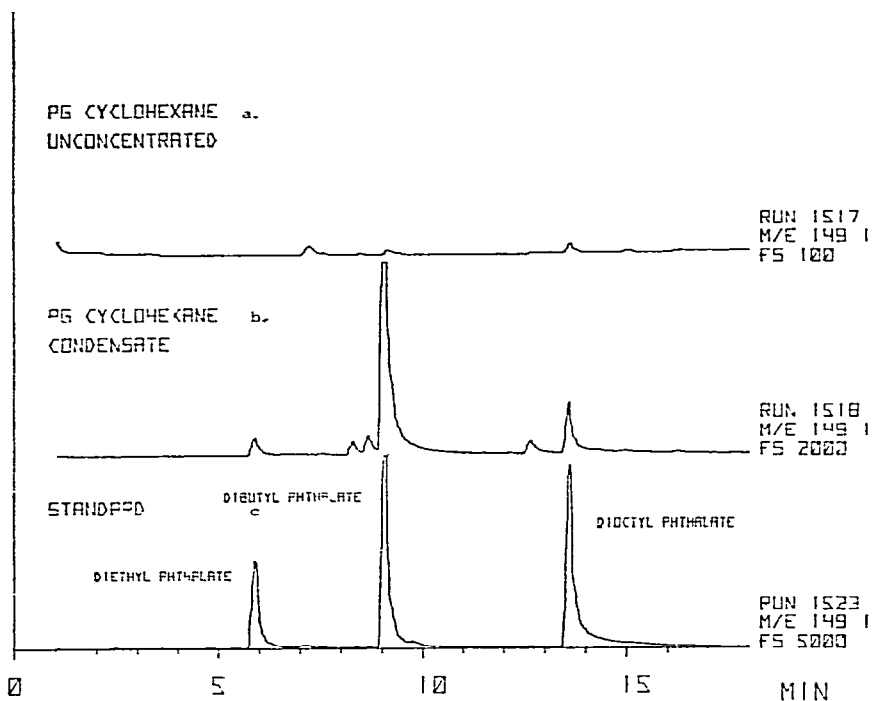Fig. 2. Plots of SIM data for PG condensate unconcentrated (procedure blank) (a), PG condensate concentrated 2000 fold (b) and GCCAL solution (c).

TABLE III

IDENTITIES AND CONCENTRATIONS OF ORGANIC COMPOUNDS IN SOLVENTS BY SIM

	CAL		BJ		PG	
	Compound	ng/ml	Compound	ng/ml	Compound	ng/ml
Cyclohexane	Dibutyl phthalate	0.1	Dibutyl phthalate	0.5	Dimethyl phthalate	<0.1
	Dioctyl phthalate	<0.1	Dioctyl phthalate	0.2	Diethyl phthalate	0.4
			Tetracosane	0.1	Dibutyl phthalate	7
			Pentacosane	0.2	Dioctyl phthalate	1
			Hexacosane	0.2		
			Heptacosane	0.2		
			Octacosane	0.2		
			Nonacosane	0.1		
			Triacontane	0.1		
Methylene chloride	Dibutyl phthalate	0.2	Dibutyl phthalate	0.9	Dimethyl phthalate	<0.1
	Dioctyl phthalate	0.2	Dioctyl phthalate	0.2	Diethyl phthalate	0.1
					Dibutyl phthalate	0.7
					Dioctyl phthalate	11
Methanol	Dibutyl phthalate	0.4	Dibutyl phthalate	0.1	Dimethyl phthalate	<0.1
	Dioctyl phthalate	0.2	Dioctyl phthalate	0.1	Diethyl phthalate	0.1
					Dibutyl phthalate	1
					Dioctyl phthalate	0.6

Methylene chloride

Results from GC analyses of condensates of CAL, BJ and PG methylene chloride are presented in Fig. 3 and the estimated concentration levels of organic compound impurities are given in Table I. In Fig. 3a no detectable components were detected by GC–FID in the CAL condensate, but three compounds were detected at retention indices of 2200, 2350 and 3040 in the BJ condensate which is shown as a GCPLOT in Fig. 3b. The first two of these components which were detected in each of three replicate analyses of BJ condensate were identified from mass spectra as diethyl phthalate at 0.5 ng/μl and dibutyl phthalate at 7.7 ng/μl uncondensed solvent. The third component at retention index 3040 was unidentified.
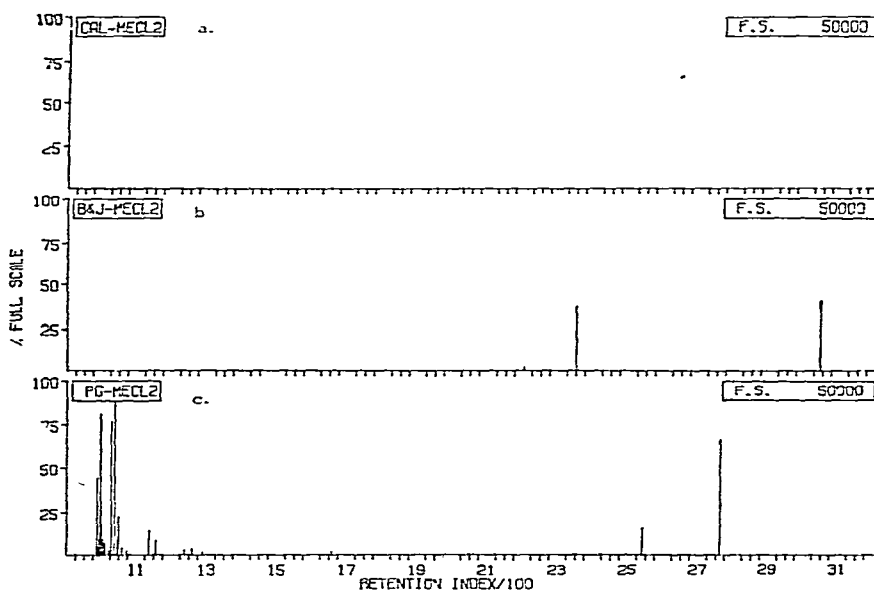

Fig. 3. GCPLOT of data from GC–FID analyses of methylene chloride condensates of CAL (a), BJ (b) and PG (c) solvents.

The GCPLOT for PG condensate is shown in Fig. 3c and summary of data from the GC–MS analysis of PG condensate is included in Table II. Approximately 22 components were detected by GC–FID, although most of these components eluted before tridecane and very near the solvent peak. Some other components eluted during the solvent time-out period in GC–MS analysis and therefore were not identified. Impurities in the PG solvent were identified using mass spectra and included chlorinated low-molecular-weight hydrocarbons such as tri- and tetrachloropropanes, tetrachloroethane, phthalic anhydride and dioctyl phthalate.

Results from SIM analyses of the methylene chloride condensates are given in Table III. Only phthalate esters were detected in any methylene chloride condensate, however total phthalate esters in PG solvent exceeded concentrations of the same compounds in distilled-in-glass grade solvent by a factor of ten.

Methanol

Results from GC analysis of condensates of CAL, BJ and PG methanol are presented in Fig. 4 and estimated concentrations of organic impurities in uncondensed solvent appear in Table I. The distilled-in-glass grade methanol solvents have only a few minor impurities, which eluted on the solvent tail and which present no serious interferences in GC or GC–MS analyses. No components were detected in GC–MS analysis of the BJ and CAL methanol condensate (Table II). Concentration levels for organic compound impurities in PG methanol were greater than concentration levels of similar impurities in distilled-in-glass grade methanol, but the concentration levels of impurities in PG methanol were much lower than concentration levels of impurities in condensates of PG cyclohexane or PG methylene chloride. Six components were detected in the GC–FID analysis of PG condensate at retention indices of 1085, 1265, 1310, 1380, 1475 and 2560. The last five components were detected during analysis by GC–MS but the component at retention index of 1085 eluted during the solvent time-out period. The next two eluting components, which were identified from mass spectra were C_8H_{12}, 1,4-bis(methylene)cyclohexane (1265) and $C_8H_{14}O$, 2,6-dimethylphenol (1475), but mass spectra of the three remaining compounds (1310, 1380, 2560) were very weak in abundance and identifications were not made.
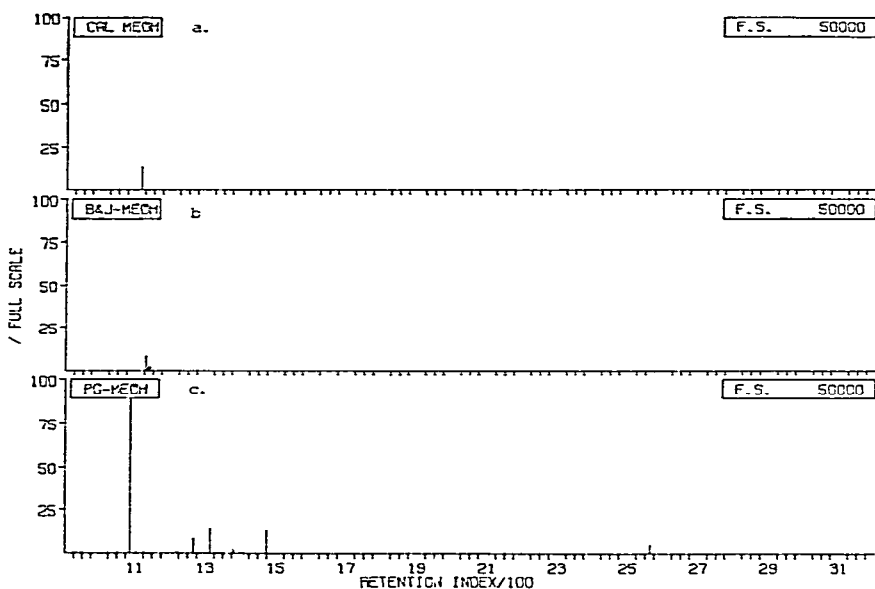

Fig. 4. GCPLOT of data from GC–FID analyses of methanol condensates of CAL (a), BJ (b) and PG (c) solvents.

Analysis of the PG condensate using SIM also showed the presence of phthalate esters at 0.1–1 ng/ml uncondensed solvent, however the number and relative concentrations of phthalate esters in the methanol also differed between PG and distilled-in-glass grades.

The study which compared qualitatively and quantitatively the impurities present as organic compounds in these solvents of two grades serves to emphasize the

importance of closely monitoring impurity levels in solvents used in trace analyses. The actual solvent chosen for a paricular application depends upon several factors including solvent cost, concentration of impurities and types of impurities. The use of procedure blanks where every step of the procedure is reproduced but without sample is important, particularly when these solvents are used in extractions of organic compounds at low concentration levels in environmental samples and the concentrates analyzed by GC, GC–MS and SIM. These artifacts if not determined may lead to erroneous conclusions regarding sample composition. Although two to four replicates of each solvent were analyzed in this study, no data concerning impurities found in different bottles or batches of solvents are reported here.

The two distilled-in-glass grades were comparable and contained fewer and lower concentrations of impurities than PG solvents. Since all of the tested solvents were received in amber glass containers having either PTFE inserts in the container cap (Caladon and PG solvents) or complete PTFE caps (BJ), it is expected that the impurity levels (detected in these various solvents) should remain constant. However, many solvents may be obtained in containers which have screw-caps with metal-foil liners and the impurity levels for these solvents may increase significantly with time[3].

REFERENCES

1   F. W. Karasek, D. W. Denney, K. W. Chan and R. E. Clement, *Anal. Chem.*, 50 (1978) 82.
2   G. A. Eiceman, R. E. Clement and F. W. Karasek, *Anal. Chem.*, 51 (1979) 2343.
3   D. W. Denney, F. W. Karasek and W. D. Bowers, *J. Chromatogr.*, 151 (1978) 75.
4   N. M. Sinclair and B. E. Frost, *Analyst (London)*, 103 (1978) 1199.
5   W. Cautreels and K. van Cauwenberghe, *Water, Air, Soil Pollut.*, 6 (1976) 103.
6   R. J. Levins, *Chromatographia*, 11 (1978) 736.
7   A. di Domenico, F. Merli, L. Boniforti, I. Camoni, A. DiMuccio, F. Taggi, L. Vergori, G. Colli, G. Elli, A. Gorni, P. Grassi, G. Invernizzi, A. Jemma, L. Luciani, F. Cattabeni, L. De Angelis, G. Galli, C. Chiabrando and R. Fanelli, *Anal. Chem.*, 51 (1979) 735.
8   J. M. Daisy and M. A. Leyko, *Anal. Chem.*, 51 (1979) 24.
9   M. D. Erickson, L. C. Michael, R. A. Zweidinger and E. D. Pellizzari, *Environ. Sci. Technol.*, 12 (1978) 922.
10 C. Golden and E. Sawicki, *Anal. Lett.*, A11 (1979) 24.
11 J. Janak, F. Onuska and S. Duras, *Chem. Prum.*, 18 (1968) 33.
12 Y. A. Prikhod'ko, M. S. Kozlova and N. I. Komyakova, *Zavod. Lab.*, 35 (1969) 157.
13 B. Hampel and K. Maas, *Chem.-Ztg. Chem. Appl.*, 95 (1971) 316.
14 E. T. Shepelev and T. A. Mindrina, *Khim. Prom-st., Ser. Metody Anal. Kontrolya kach. Prod. Khim. Prom-sti.*, 7 (1979) 5.
15 V. G. Berezkin and M. N. Budantseva, *J. Chromatogr.*, 191 (1980) 309.
16 M. Ishida, K. Suyama and S. Adachi, *J. Chromatogr.*, 189 (1980) 421.
17 C. R. Hastings and W. A. Aue, *J. Chromatogr.*, 89 (1974) 369.
18 H. H. Hill, Jr., K. W. Chan and F. W. Karasek, *J. Chromatogr.*, 131 (1977) 245.
19 S. R. Heller and G. W. A. Milne, *EPA/NIH Mass Spectral Data Base*, NSRDS-NBS 63, U.S. Govn't Printing Office, Washington, DC, 1978.
20 *Eight Peak Index of Mass Spectra First Edition*, Mass Spectrometry Data Centre, Reading, 1970.
21 *NIH/EPA CIS Project*, Interactive Sciences Corp., Washington, DC.
22 R. E. Clement, *M.Sc. Thesis*, Univ. of Waterloo, Waterloo, August 1976.