Journal of Chromatography, 207 (1981) 203–211
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 13,420

COMPONENT LOSS DURING EVAPORATION–RECONSTITUTION OF ORGANIC ENVIRONMENTAL SAMPLES FOR GAS CHROMATOGRAPHIC ANALYSIS

W. D. BOWERS and M. L. PARSONS*
Arizona State University, Department of Chemistry, Tempe, AZ 85281 (U.S.A.)
and
R. E. CLEMENT and F. W. KARASEK
The Guelph-Waterloo Center For Graduate Work in Chemistry, Waterloo Campus, Department of Chemistry, Waterloo, Ontario N2L 3G1 (Canada)
(Received October 14th, 1980)

SUMMARY

Standard and sample solutions stored in borosilicate sample vials were allowed to evaporate to dryness at room temperature. The solutions were analyzed by gas chromatography–flame ionization detection before evaporation and after reconstitution to the original volume to determine component losses due to evaporation. The standard solutions were also stored in sample vials which had been treated with a surface deactivating agent, benzyltriphenylphosphonium chloride. The standard solution contained *n*-hydrocarbons, 1-alcohols, phthalates and polynuclear aromatic hydrocarbons. The sample solution was a benzene extract of municipal incinerator fly-ash which contained over 200 components including *n*-hydrocarbons, phthalates, polynuclear aromatic hydrocarbons and polychlorinated dibenzo-*p*-dioxins. At the 95% confidence level, the differences among mean losses observed with the 100 ng/μl standard mixture were within random variations between untreated and deactivated vials. The random variations between mean losses of the 10 ng/μl mixture were significantly higher with the deactivated vials at the 99% confidence level. Large losses were observed for early-eluting components of the standard solutions and the benzene extract of incinerator fly ash. Losses for polychlorinated benzo-*p*-dioxins and polynuclear aromatic hydrocarbons averaged *ca.* 10%.

INTRODUCTION

Because of the high toxicity of certain substances, it is necessary to detect their presence in the environment at trace-to-ultratrace levels. These substances are usually present in mixtures containing a large number of components. The use of multi-step sample preparation and clean-up procedures in which the sample is taken to dryness and reconstituted before analysis is common[1,2]. The use of these procedures can result in the introduction of artifacts and loss of sample components. Karasek *et al.* have

0021-9673/81/0000–0000/$02.50

reported a rapid and simple procedure for the analysis of complex organic mixtures extracted from airborne particulate matter[3] and municipal incinerator fly ash[4] in which the sample clean-up steps are not necessary. Care is taken to prevent the sample extract from achieving dryness throughout the sample preparation procedure.

The method of reducing sample extracts to dryness and reconstituting to the final desired volume has been described[5–9]. It has been shown that significant losses result when pesticide residue extracts are evaporated to dryness before analysis[10,11]. Burke *et al.*[10] have investigated various concentration procedures used to bring samples to dryness and reported that losses were observed when the extract was concentrated to less than 500 μl, independently of the concentration procedure used. Chiba and Morley[11] reported that the use of petroleum ether as the extraction solvent resulted in greater losses upon condensation of the extract compared to benzene. In their study, detectable sample loss was observed even when a viscous retaining agent, such as ethylene glycol was used, when reducing the organic extract below 500 μl.

Although the Pyrex glassware generally used in trace analysis is considered inert, this surface has been observed to exhibit an undesirable activity towards polar compounds, owing to the presence of boron, potassium, and silanol groups in the glass matrix[12,13]. These active sites have been shown to adsorb polar compounds totally[13–15]. A common surface deactivation procedure is silylation. However, this only reacts with the silanol groups allowing the active metal sites to remain. Surface-active agents have been shown to be more effective in the deactivation of the entire glass surface towards polar compounds[12,15,16,18].

Studies reported to date which deal with sample component losses during concentration procedures have been primarily concerned with pesticide residues. Also, few data have been presented to show actual losses for other real samples, since most results have been obtained from standard solutions. As yet, no comprehensive study has been reported in which a large range of solvent– and sample–matrix systems have been investigated. This study was conceived to examine and compare component losses from mixtures containing a variety of compound types when evaporated to dryness and reconstituted. Component losses were investigated employing standard borosilicate sample vials, some of which were coated before use with benzyltriphenylphosphonium chloride (BTPPC) to achieve surface deactivation. Lowering the adsorptive properties of the glass surface might result in a greater recovery of sample components. Mixtures studied include a standard solution containing *n*-hydrocarbons, phthalates, polynuclear aromatic hydrocarbons (PAHs) and primary alcohols in cyclohexane as well as a benzene extraction of municipal incinerator fly ash. Of particular interest are the polychlorinated dibenzo-*p*-dioxins (PCDD), since some reported methods for their analysis require evaporation to dryness of sample extracts[1,2].

EXPERIMENTAL

The concentrated standard solution used contained *n*-hydrocarbons, 1-alcohols, PAHs and phthalates in cyclohexane solvent. A dilute standard was prepared by a 1:10 dilution of the solution given in Table I. Straight-chain hydrocarbons and alcohols were from standard kits (Poly-Science, Niles, IL, U.S.A.), dioctyl phthalate was Baker "Practical Grade" (J. T. Baker, Phillipsburg, NJ, U.S.A.) and the other

phthalates were from Matheson, Coleman and Bell (Norwood, OH, U.S.A.) and PAHs were obtained from Aldrich (Milwaukee, WI, U.S.A.). Cyclohexane (Burdick & Jackson Labs., Muskegon, MI, U.S.A.) and benzene (Caledon Labs., Guelph, Canada) were "distilled-in-glass" grade. The BTPPC (Research Org./Inorg. Chem. Corp., Belleville, NJ, U.S.A.) surface-active agent was a 1% solution in methylene chloride ("distilled-in-glass" grade, Burdick & Jackson Labs.).

Storage containers used were Reacti-vials™ (Chromatographic Specialities, Brockville, Canada) equipped with screw-caps and PTFE liners. Before use, all glassware was cleaned by ultrasonic vibration in an aqueous solution of Alconox detergent (Alconox, New York, NY, U.S.A.), rinsed with copious amounts of tap water, rinsed thoroughly with deionized water, and heated in a laboratory oven for 1 h at 300°C. Glassware was allowed to cool to room temperature before use.

Vials to be deactivated were each coated five times with a 1% solution of BTPPC in methylene chloride. After each coating the vials were inverted and allowed to dry before the next application of BTPPC. All vials used in the study appeared to have even coatings.

Standard solutions

The experimental procedure followed for the standard mixtures is outlined in Fig. 1. A 1-ml volume of the concentrated (100 ng/μl) standard was placed into each of the four vials (two deactivated, two untreated). The dilute (10 ng/μl) standard was treated in the same manner. The original standard solutions were stored in a freezer at *ca.* −15°C. The solutions in the vials were allowed to evaporate to dryness by storing at room temperature in a fume hood with the screw-caps loosely fastened. The mixtures achieved dryness after *ca.* 20 h, and all vials were observed to have a yellow-brown residue which remained after evaporation. The standard solutions were then reconstituted by addition of 1 ml of cyclohexane. All vials were then agitated ultrasonically for *ca.* 1 min to promote homogeneity and redissolution of the organic residue. There appeared to be no residue after ultrasonic agitation.

Incinerator fly ash extract

The experimental procedure followed for the benzene extract of municipal incinerator fly ash is outlined in Fig. 2. The fly ash was supplied by the Ontario Ministry of the Environment and consisted of grab samples from municipal incinerators located in urban centers in southern Ontario. The fly ash, 116 g, was extracted with benzene using ultrasonic agitation. Initially, the fly ash was placed in a round-bottomed flask with 300 ml benzene and agitated for 30 min. After decanting the benzene through a medium-porosity glass-fritted filter, 100 ml of additional benzene was added and the 30 min extraction cycle was repeated. A total of four extraction cycles were used employing a total of 600 ml. After the last cycle the fly ash was transferred to the glass-fritted filter and rinsed with 50 ml of fresh benzene, and the sorbed fly ash extract was recovered by aspirator suction. The benzene extract was concentrated to a final volume of 800 μl by rotary evaporation and stored in a 1.0-ml vial equipped with screw-cap and teflon liner from which the 100-μl portions were taken for the sample evaporation study.

To each of two untreated vials was added 100 μl (Fig. 2). The remaining extract was stored in a freezer at *ca.* −15°C. The vials were allowed to evaporate to

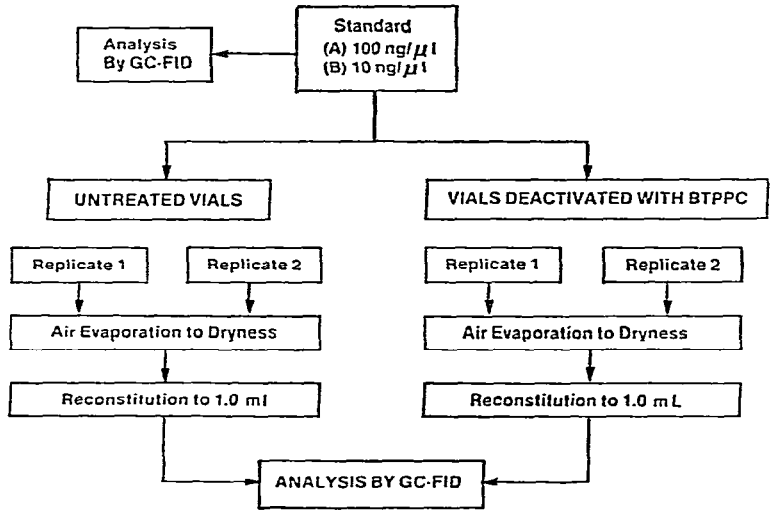

Fig. 1. Schematic of experimental procedure followed for the standard mixtures.

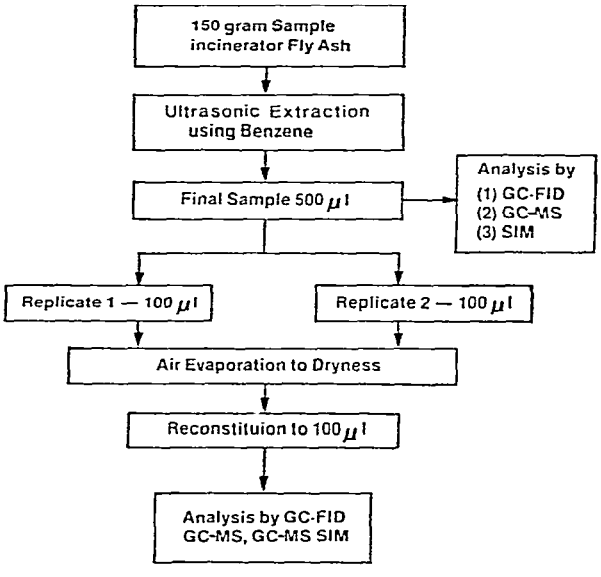

Fig. 2. Schematic of experimental procedure followed for the benzene fly ash extract.

dryness by storing at ambient temperatures in a fume hood with screw-caps loosely fastened. The extracts achieved dryness after *ca.* 40 h, and both vials were observed to have a yellow-brown residue. Each vial was then reconstituted by addition of 100 μl of benzene and then ultrasonically agitated for 1 min.

After reconstitution, all samples were analyzed by gas chromatography–flame ionization detection (GC–FID), using a Hewlett-Packard 5830A GC equipped with 1.8 m × 2 mm I.D. glass column packed with Aue packing[16]. Analysis conditions

were as follows: initial temperature, 90°C; program rate, 4°C/min; final temperature, 250°C, held for 15 min; injection port, 250°C; FID temperature, 275°C; helium carrier flow, 40 ml/min; injection volume, 3 μl. The initial temperature for the benzene sample condensates was 50°C. Original standards stored in the freezer were chromatographed under the same conditions for comparisons.

In addition to GC–FID analysis, original and reconstituted benzene condensates were analyzed by a Hewlett-Packard 5992 GC–MS–calculator system. GC conditions were as above with an initial temperature of 90°C. The GC–MS was operated in selected-ion-monitoring (SIM) mode, in which the quadrupole MS was selected tuned to each of six chosen ions during a single analysis. Compounds monitored were phthalates (ion 149.1), *n*-hydrocarbons (ion 85.1), biphenyl (ion 154.1), fluorene (ion 166.1), fluoranthene and pyrene (ion 202.2), anthracene (ion 178.1) and benzopyrene (ion 252.2). Various PCDD isomer series were also monitored, including the tetra (ion 321.9), penta (ion 355.9), hexa (ion 389.9) and hepta (ion 425.8) isomers, and octachlorodibenzo-*p*-dioxin (ion 459.7).

RESULTS AND DISCUSSION

Evaporation–reconstitution of standard mixtures

The loss of each component in the 100 ng/μl. standard mixture following evaporation–reconstitution is given in Table I. Comparison between the average integrated area of each component in the original mixture and the areas after the evaporation–reconstitution step was made to arrive at the amount of each component lost. The variance between the average mean losses of the deactivated and untreated vials were within random variations at the 95% confidence level. Variances were also compared between the first eight eluting components for both vials since they showed greater losses, and were within random variations at the 95% confidence level. This is also reflected by the average total loss from each type of vial which are within the injection and instrument variation of ±3.1%.

The results of the evaporation–reconstitution procedure for the 10 ng/μl standard mixture are given in Table II. The first three eluting components were entirely lost by both vial types. The average mean losses between the deactivated and untreated vials were not within random variations at the 99% confidence level. This is an indication that the untreated vials were more reproducible in component loss following the evaporation step. The variations of the first eight eluting components were also greater for the deactivated vials at the 95% level, but the rest of the components were barely within the random variations at the 95% confidence level. The variability of the vials coating of BTPPC could be the major case of this observation.

Several deactivated vial values in Table II are reported as positive and correspond to a net gain in each component. These are due to random variations and are within the ±1.8% variation of injection and instrument fluctuations obtained from replicate injections of the original 10 ng/μl standard mixture. Comparisons of the average total loss observed for the deactivated and untreated vials indicates a significantly larger loss from the untreated vials. However, due to the large variance in the component recovery of the deactivated vials it is difficult to show that the use of deactivated vials will result in a lower loss of components.

TABLE I

COMPONENT LOSS AFTER EVAPORATION–RECONSTITUTION OF 100 ng/μl STANDARD SOLUTION

Component	*Retention time (min)*	*Original solution (ng/μl)*	*Loss (ng/μl)*			
			Deactivated No. 1	*Deactivited No. 2*	*Untreated No. 1*	*Untreated No. 2*
Biphenyl	3.6	126	66	63	61	50
Fluorene	7.7	102	28	28	30	21
Dimethyl phthalate	8.4	134	36	40	42	31
Octadecane	9.4	99	12	17	21	13
Diethyl phthalate	10.6	101	17	21	24	15
Tetradecanol	11.4	103	11	16	21	13
Eicosane	13.8	103	8	14	19	13
Hexadecanol	15.8	102	8	15	19	12
Dibutyl phthalate	18.0	102	8	14	19	12
Fluoranthene	20.0	111	11	17	21	16
Tetracosane	22.0	103	9	13	17	11
Eicosanol	23.7	104	13	15	18	11
Hexacosane	25.8	102	10	13	17	11
Dioctyl phthalate	28.9	101	6	13	17	10
Triacontane	32.8	100	6	11	16	11
Benzo[*a*]pyrene	35.9	100	11	16	15	11
Total loss (ng/μl)			260	326	377	261

TABLE II

COMPONENT LOSS AFTER EVAPORATION–RECONSTITUTION OF 10 ng/μl STANDARD SOLUTION

Component	*Retention time (min)*	*Original solution (ng/μl)*	*Loss (ng/μl)*			
			Deactivated No. 1	*Deactivated No. 2*	*Untreated No. 1*	*Untreated No. 2*
Biphenyl	3.6	12.6	12.6	12.6	12.6	12.6
Fluorene	7.7	10.2	10.2	10.2	10.2	10.2
Dimethyl phthalate	8.4	13.4	13.4	13.4	13.4	13.4
Octadecane	9.4	9.9	2.3	3.3	2.3	2.8
Diethyl phthalate	10.6	10.1	5.0	6.9	5.1	4.8
Tetradecanol	11.4	10.3	0.9	3.0	2.0	2.6
Eicosane	13.8	10.3	+0.8*	1.5	0.8	1.4
Hexadecanol	15.8	10.2	+0.4	1.5	1.0	2.0
Dibutyl phthalate	18.0	10.2	+1.2	0.8	0.4	1.1
Fluoranthene	20.1	11.1	+0.3	2.1	1.4	2.1
Tetracosane	22.0	10.3	+1.0	0.5	0.6	1.2
Eicosanol	23.7	10.4	+1.3	0.5	0.7	1.5
Hexacosane	25.8	10.2	+1.1	0.4	0.6	1.2
Dioctyl phthalate	28.9	10.1	+1.0	0.5	0.5	1.0
Triacontane	32.5	10.0	+0.9	+0.1	1.3	1.8
Benzo[*a*]pyrene	36.0	10.0	0.1	2.3	1.3	1.6
Total loss (ng/μl)			36.5	59.4	54.2	61.3

* Positive value indicates a net gain in the component after evaporation–reconstruction.

Evaporation–reconstitution of fly ash extract

Fig. 3 is a comparison between the GC–FID results obtained for the original fly ash extract and one of the fly ash replicates after evaporation–reconstitution.

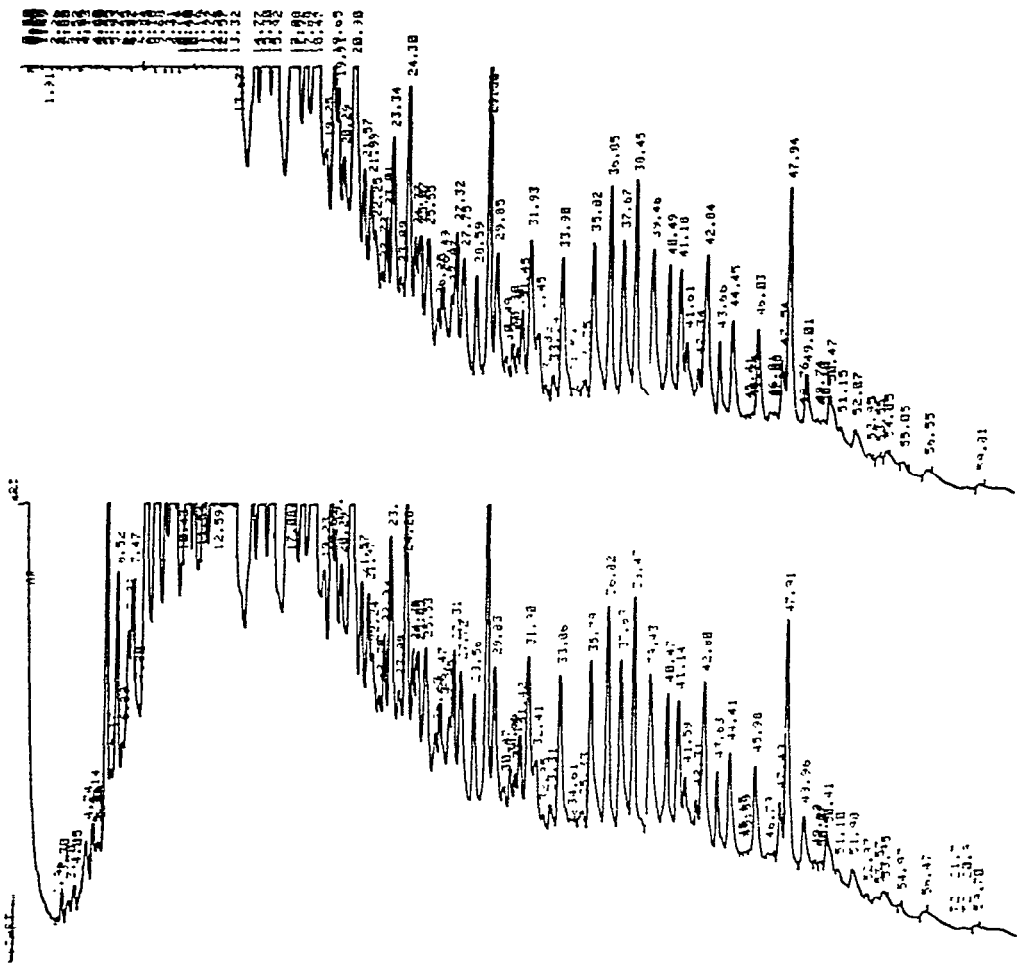

Fig. 3. Comparison of GC–FID results for 3-μl injections of: original fly ash extract (top), and the same extract after evaporation–reconstitution.

Although the two chromatograms are very similar for components which elute after a retention time of *ca.* 13 min, significant losses of earlier-eluting compounds can be observed in the reconstituted sample. Table III summarizes the GC–FID results for the original and evaporated–reconstituted replicates. Since peak areas can be related to amounts of substances through response factors, the data in Table III are a direct indication of the relative amounts of organic material detected.

Results of GC–MS analysis using SIM are given in Table IV. Reported recoveries for compounds in Table IV are based on comparisons between the average

TABLE III

GC–FID TOTAL AREAS* OF FLY ASH EXTRACT CONDENSATE BEFORE AND AFTER EVAPORATION–RECONSTITUTION

	Before evaporation to dryness		*After evaporation–reconstitution*	
	Replicate I	*Replicate II*	*Replicate I*	*Replicate II*
Early-eluting components (<retention index 1400)	6516	8717	567	932
Late eluting components (>retention index 2500)	200	205	190	265
Total area	7579	10,000	3274	3797

* Areas are summations of total areas of all peaks detected and are normalized to largest total peak area = 10,000.

TABLE IV

RECOVERIES OF SELECTED COMPOUNDS AFTER EVAPORATION–RECONSTITUTION OF BENZENE EXTRACTION OF INCINERATOR FLY ASH

Compound	*Recovery (%)*	
	Replicate I	*Replicate 2*
n-Hydrocarbons (C_{14}–C_{30})	99	87
Diethyl phthalate	91	87
Dibutyl phthalate	92	91
Dioctyl phthalate	86	89
Biphenyl	67	62
Pentachlorobenzene	95	97
Fluorene	92	82
Anthracene	95	90
Fluoranthene	96	96
Pyrene	91	88
Benzopyrene	90	98
Tetrachlorodioxins	91	88
Pentachlorodioxins	89	86
Hexachlorodioxins	91	87
Heptachlorodioxins	97	80
Octachlorodibenzo-*p*-dioxin	90	80

integrated areas for two replicate injections of the original fly ash extract and the areas each of the evaporated–reconstituted samples. For the chlorinated dioxins, the total integrated areas for particular isomer series were compared. Identities of all of the compounds which are listed in Table IV were known by their mass spectra and correspondence of retention times of standards from previous work[4]. The average percentage deviation of areas from calculated means for the two non-evaporated samples was $\pm 2.3\%$, ranging from $\pm 0.02\%$ for biphenyl to $\pm 6.2\%$ for pentachlorobenzene. The corresponding average for the two evaporated–reconstituted replicates was $\pm 3.1\%$, which ranged from $\pm 0.2\%$ for fluoranthene to $\pm 10\%$ for the heptachlorodibenzo-*p*-dioxins. Percentage losses were less for the fly ash extract than for the standard solution for compounds common to both of these tests. Average

percentage losses for the standard solution were 15 ± 2, 16 ± 3 and 18 ± 6 for the *n*-hydrocarbons, phthalates and PAH compounds in the mixture, respectively. Corresponding average losses of 7 ± 3, 10 ± 2 and 8 ± 5% were observed for the corresponding *n*-hydrocarbons, phthalates and PAH which were detected in the fly ash extract. Biphenyl losses were not included in the above figures. They averaged 44% in the standard solution and 35% in the fly ash extract.

Most recoveries in Table IV are *ca.* 90%. The lowest recovery was achieved for biphenyl (65%), which is the lowest boiling compound of those in Table IV. These results indicate that bringing a sample to dryness may result in significant losses of extracted organics. Losses were observed even for high molecular weight components such as benzopyrene and the various chlorinated dioxin isomers. Since these samples were allowed to evaporate under very gentle conditions, lower recoveries may be expected when bringing a sample extract to dryness under conditions of reduced pressure and greater than ambient temperature. For this study, no sample transfer steps were involved other than the initial transfer of the stock solution to the sample vials. Further losses can be expected during regular sample analysis which may include several transfer steps and sample clean-up procedures.

ACKNOWLEDGEMENT

This work was supported by the Environmental Protection Agency, Grant No. R-807028-01.

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