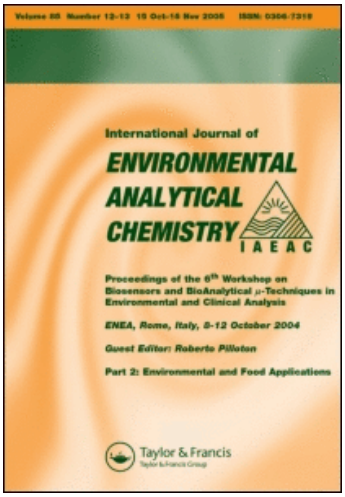

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A Study on Losses of PAHs During Sample Concentration for Chromatographic Analysis: Evaporation with a Stream of Nitrogen

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A STUDY ON LOSSES OF PAHS DURING SAMPLE CONCENTRATION FOR CHROMATOGRAPHIC ANALYSIS: EVAPORATION WITH A STREAM OF NITROGEN

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Losses of polynuclear aromatic hydrocarbons (PAHs) in methylene chloride during evaporation with a stream of nitrogen was systematically studied. The starting sample concentration levels were 0.167 μg/mL and 0.00333 μg/mL for each PAH. These two sets of test solutions were both evaporated from 300 mL to final volumes of 50, 30, 5, 3, and 1 mL, with a constant stream of nitrogen and in a water bath kept at 40°C. Each sample was analyzed by GC-FID.

Factors affecting the percentage of analyte recovery include boiling points of analytes, the final sample volume and the starting sample concentration. When the diluted solutions were reduced from 300 mL to 1 mL, the recoveries for PAHs were all higher than 90%. However, when the concentrated solutions were evaporated to 1 mL, recoveries of all analytes dropped below 85%, and naphthalene, the most volatile PAH, dropped to 77.5%. If evaporation was halted to a final volume of 3~5 mL, the recovery for PAHs in both concentrated and diluted solutions were still almost all higher than 90%. This implies that during evaporation of methylene chloride with a nitrogen stream, no significant losses of semivolatile analytes, regardless of their boiling points or concentration levels, were found until or unless the final volume reaches below 3~5 mL. Apparently, the solute losses are mainly due to coevaporation instead of vapor partition.

Keywords: PAH; concentration; evaporation; nitrogen; Kuderna-Danish

INTRODUCTION

Analytical methods for determining semivolatile analytes, such as polynuclear aromatic hydrocarbons (PAHs), usually require environmental samples containing trace amount of analytes be first concentrated by stripping off most of the

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solvent in order to make analysis effective. In the field of environmental analysis, the concentration methods commonly used include: purging with a gentle stream of nitrogen gas,[1,2] evaporation in a set of Kuderna-Danish (K-D) apparatus,[3,4] concentration with a rotary evaporator[5,6] or a combination of the above.[7,8] The nitrogen concentration approach is particularly attractive owing to its ease of use. It requires only simple equipment and is especially applicable at the final stage of a concentration procedure. Therefore, it has been widely used in PAH analysis.

During the past thirty-five years, investigators discussed the losses of analytes during sample preparation using various concentration techniques. Burke et al.[9] and Chiba et al.[10] evaluated different concentration techniques. They both showed that large losses of pesticide occurred when the solutions of pesticide were evaporated to the volumes of 0.5 mL or less. Bowers et al.[11] indicated that under very gentle conditions of air evaporation, percentage losses for the standard solution (incinerator fly ash) were 15 ± 2, 16 ± 3 and 18 ± 6 for the n-hydrocarbons, phthalates and PAH compounds, respectively. Furthermore, another study reported by Ferreira et al.,[12]using the micro-Kuderna-Danish concentrator, showed that solute losses were mainly due to the flushing of solute layers from dry surfaces (coevaporation) during the final sample evaporation step (below 0.5 mL). Another Ferreira study,[13] discussing the losses of a series of organic compounds evaporated with a stream of nitrogen, has been, of recent, the more interesting issue. However, little literature evaluating systematically and in detail the impact of the nitrogen concentration step on the analytical quality of the final results for PAH analysis has been reported.

The work described here was designed to investigate PAH losses when using nitrogen evaporation. Further, the work attempted to derive conclusions about the characteristics of nitrogen evaporation.

EXPERIMENTAL

Chemicals

Throughout the study analytical-reagent grade methylene chloride (dichloromethane, DCM) from Merck (Darmstadt, Germany) as the solvent, and perylene-d_{12} from Supelco (Bellefonte, PA, U.S.A.) at a concentration of 2000 μg/mL as the internal standard were used. Methylene chloride was further distilled before use. The PAH standard from Supelco (product name: TCL Polynuclear Aromatic Hydrocarbons Mix) contains the following compounds (listed in the order of increasing retention time), each at a concentration of 2000 μg/mL: naph-

thalene (Nap), acenaphthylene (AcPy), acenaphthene (Acp), fluorene (Flu), phenanthrene (PA), anthracene (Ant), fluoranthene (FL), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IND), dibenz[a,h]anthracene (DBA) and benzo[ghi]perylene (Bghip).

Gas chromatographic analysis

PAH analyses were performed using a Hewlett Packard (HP) 6890 gas chromatograph (GC). The GC was equipped with electronic pressure control (EPC), a programmable temperature vaporizer (PTV), a classical hot split/splitless injector and a flame ionization detector (FID). Ultra pure helium was used as the carrier gas. A HP G1513A automatic liquid sampler (ALS) with a HP G1512A controller was used for sample injection. Separation was achieved on a HP-5 capillary column (30 m × 0.25 mm, 0.25 μ m).

Two GC programs, hot splitless mode and solvent vent mode, were employed respectively for the analyses of the concentrated and the diluted PAH solutions. The detail of the programs is listed in Table I. The technique regarding solvent vent mode using PTV has been proved successful in our previous studies.[14,15]

Concentration systems

The tested samples were placed in a 300-mL evaporative glass flask (Figure 1) with a cylindrical bottom. This flask was custom-designed by and fabricated for our laboratory. The flasks were partially submerged in a water bath at 40°C. A cylinder of ultra pure nitrogen equipped with a pressure regulator was used, from which a gentle and constant stream of nitrogen gas was then, directed from above to the center of the surface of the solution. Consequently, a dimple was formed without causing any observable splash. Evaporation was allowed to continue until the desired final volume was achieved. Then the flask was removed from the system and the subsequent analysis performed.

Testing methodology

In this study, five different volumes, 1, 3, 5, 30 and 50 mL, were chosen to be the final volumes. Two sets, one set of concentrated and one set of diluted solution were prepared, 0.167 (1/6) and 0.00333 (1/300) μg/mL. All were prepared from the stock solution of 200 μg/mL PAH for each compound. Each of the two sets contained 15 solutions composed of methylene chloride solvent and dissolved

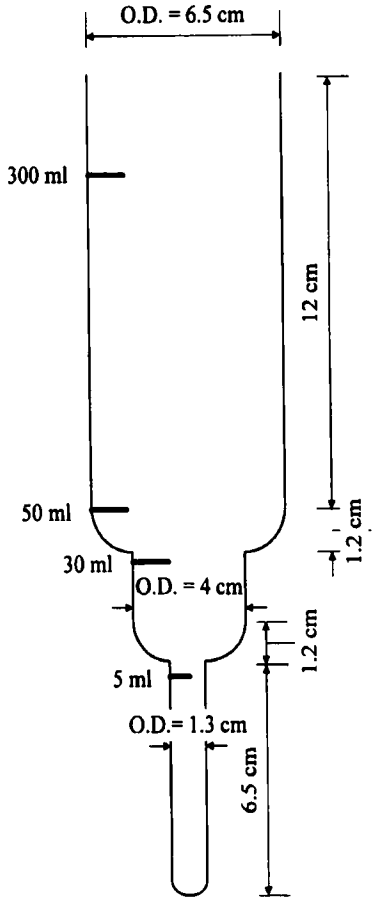

FIGURE 1 Diagram of the 300-mL evaporative glass flask used in this study (not to scale)

PAHs. Each solution was concentrated using the above mentioned nitrogen-concentration system in a thermostated bath at 40°C. Three solutions from each set were concentrated from a volume of 300 mL to 50 mL, while other groups of three, 300-mL volumes were concentrated to 30, 5, 3 and 1 mL. When each preset final volume was reached the flask was removed from the water-bath and the internal standard was added (only for the set of concentrated solutions because the internal standard would be lost using the PTV method). Lastly, the mixture was immediately transferred into an auto-sampler vial and analyzed. All chromatographic results obtained were the average of three determinations.

TABLE I GC programs for PAH analysis

Injection mode	*Conditions*
Hot splitless mode (split/splitless injector)	• Inlet: temperature: 300°C; purge flow: 100 mL/min at 5.5 min; injection volume: 1 μL
	• Oven: temperature: 50 to 220°C at 8°C/min, 2°C/min to 250°C, 10°C/ min to 290°C; carrier gas: helium
	• Detector: temperature: 325°C; H_2 flow: 45 mL/min; air flow: 450 mL/min; make-up gas: N_2
Solvent vent mode (PTV)	• Inlet: temperature: −10°C for 1 min, 100°C/min to 290 °C; vent time: 1 min, vent flow: 75 mL/min; vent pressure: 0 bar; purge flow: 100 mL/min; purge time: 5 min; injection volume: 50 μL
	• Oven: temperature: 70°C for 10 min, 8°C/min to 220 °C, 2°C/min to 280°C; carrier gas: helium
	• Detector: temperature: 325°C; H_2 flow: 45 mL/min; air flow: 450 mL/min; make-up gas: N_2

RESULTS AND DISCUSSION

Reproducibility

Experiments using the above-mentioned chemicals were conducted to determine the precision of these two injection techniques used. The three concentrations selected for hot splitless injections were 1, 10 and 50 μg/mL. Likewise, for LVI studies the concentrations of 0.02, 0.2 and 1 μg/mL were selected. Notice that the mass of solute injected in the hot splitless runs (injection volume = 1 μL) were respectively equal to those in the LVI runs (injection volume = 50 μL).

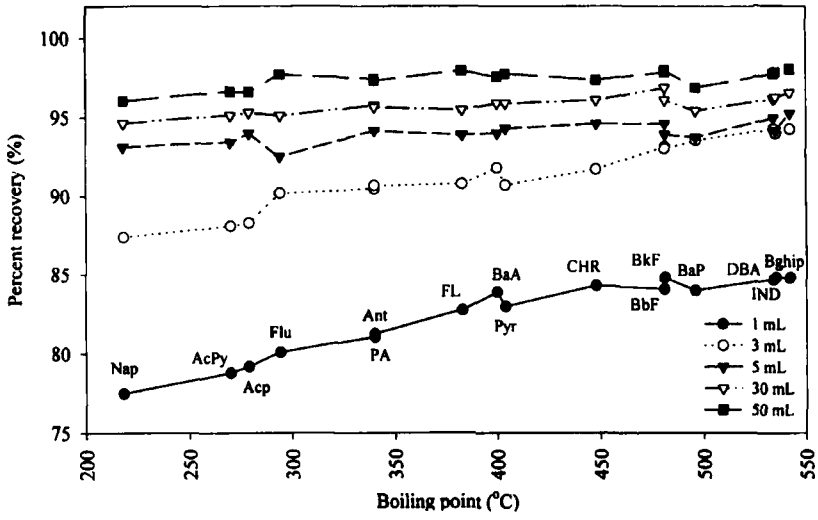

FIGURE 2 Percentage of PAHs retained in solution vs. analyte boiling point, after evaporation concentration of a concentrated solution (starting conc.=0.167 μg/mL) from a 300-mL to the desired volume (1, 3, 5, 30, 50 mL)

The precision (expressed as percent relative standard deviation, %RSD) of repeated auto-sampler injections (n = 3) is shown in Table II. From the data it is apparent that for each tested compound the precision was better than 3% for hot splitless injection (0.08~2.81%) and 8% for LVI (0.41~7.54%). Apparently, these percentages were acceptable for most trace analyses. The precision of hot splitless injection was found to be more reproducible than LVI. This result confirms that the problem of larger variations among individual compounds, which was commonly found in analyses of all diluted solutions (Figure 3).

TABLE II Precision (%RSD) of hot splitless injection and PTV

Compound	*Hot splitless (Inj. Vol.=1 μL)*			*PTV (Inj. Vol.=50 μL)*		
	1	*10*	*50*	*0.02*	*0.2*	*1*
	Concentration, μg/mL			*Concentration, μg/mL*		
Naphthalene	1.29	0.40	0.59	4.18	3.01	1.22
Acenaphthylene	1.31	0.44	0.95	2.22	1.43	1.09
Acenaphthene	2.30	0.49	0.42	6.74	1.80	1.28
Fluorene	2.81	0.55	0.35	3.23	7.54	1.27
Phenanthrene	1.44	0.59	0.36	2.82	1.94	1.08
Anthracene	1.81	0.75	0.32	4.42	2.77	1.13
Fluoranthene	1.61	0.73	0.28	2.18	0.41	0.82
Pyrene	1.48	0.68	0.30	2.79	1.15	1.68
Benz[a]anthracene	2.08	0.94	0.08	1.60	1.03	0.67
Chrysene	1.61	0.84	0.21	2.29	1.08	0.97
Benzo[b]fluoranthene	2.27	0.79	0.21	1.90	2.77	0.68
Benzo[k]fluoranthene	1.98	0.71	0.16	3.18	1.88	0.67
Benzo[a]pyrene	2.40	0.76	0.22	1.77	1.92	0.60
Indeno[1,2,3-cd]pyrene	2.15	1.11	0.60	6.59	1.81	2.21
Dibenz[a,h]anthracene	1.88	1.24	0.48	2.26	3.15	2.58
Benzo[ghi]perylene	1.29	0.89	0.46	6.60	3.32	4.11
Perylene-d_{12}	1.48	0.97	0.53	–	–	–

Study of the influence of the boiling point of analytes

Figures 2 and 3 show that the amount of analytes lost in the concentration procedure depended slightly on their boiling points. However in general, a trend revealed that the higher the volatility the higher the losses. Nonetheless, relatively constant levels of losses were maintained. Only when concentrating solutions to 1 and 3 mL were the losses of the more volatile compounds (boiling point < 300°C) significantly higher than those observed for the less volatile compounds. This phenomenon was most significant for the concentrated solutions (Figure 2). Interestingly, Ferreira's study[12] concluded that if the concentration equipment works like a distillation system (e.g., K-D concentrator), the solutes with boiling points higher than 100°C are almost all retained in the solutions.

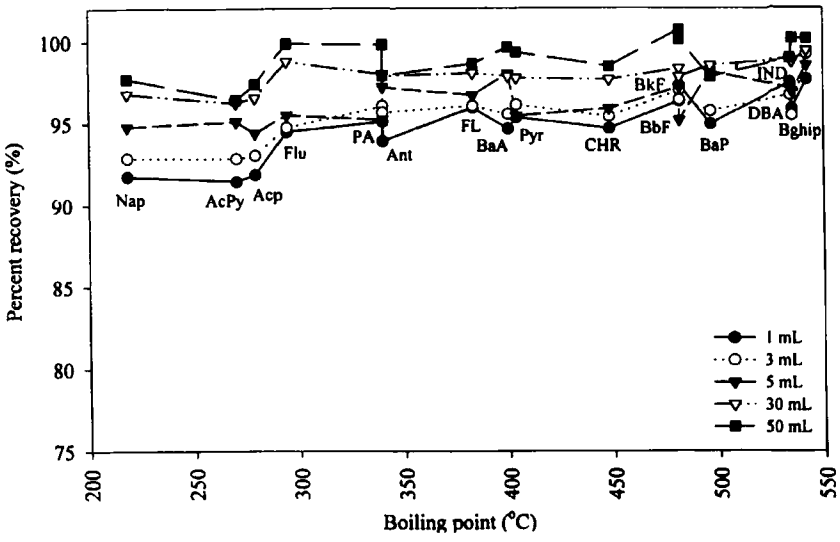

FIGURE 3 Percentage of PAHs retained in solution vs. analyte boiling point, after evaporation concentration of a diluted solution (starting conc.=0.00333 μg/mL) from a 300-mL to the desired volume (1, 3, 5, 30, 50 mL)

Therefore, if one only uses the concept of ideal vapor-liquid equilibrium, the outcome obtained here can not explain why components with very high boiling points (218~542°C) are lost at such an appreciable extent (e.g., a proportion of 22.5% of naphthalene lost when concentrating the concentrated solutions to 1 mL). In order to explain this phenomenon, we adopt the concept of coevaporation previously discussed by other researchers.[12,13,16] This concept states that if the analytes are deposited on a clean, dry glass surface with a low retention power, they will be easily carried out of the evaporating solution by the stream of ascending solvent, almost regardless of their boiling points.[13] The most volatile compounds are lost due to both vapor partition and coevaporation, while the less volatile compounds are lost mainly due to coevaporation.

Study of the influence of the final volume reached

After evaporating the concentrated solutions (starting concentration = 0.167 μg/mL) from 300 mL down to 1 mL, the percent recoveries (± standard deviation) of individual compounds ranged from 77.5 ± 5.0% (naphthalene) to 84.8 ± 2.8% (benzo[ghi]perylene) with a mean percentage of 82.5 ± 4.3%, and the corresponding standard deviations were between 2.2% and 6.7% (Figure 2). We also

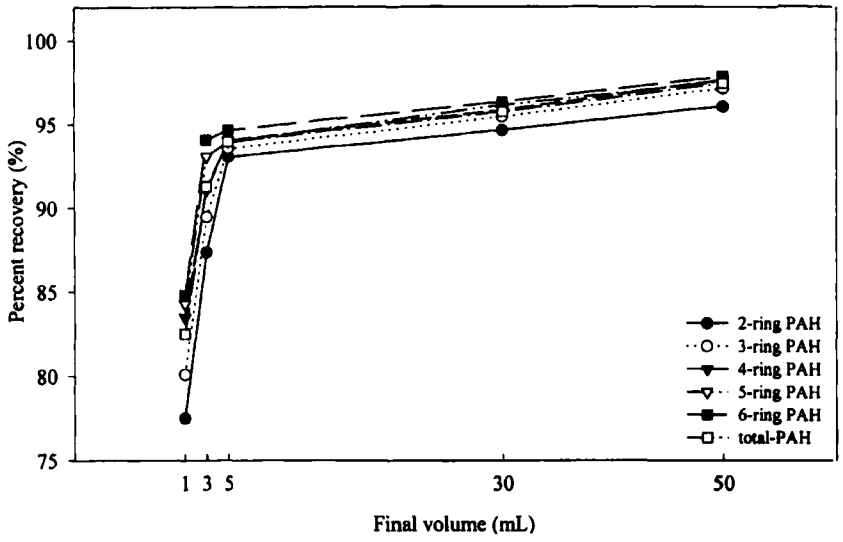

FIGURE 4 Percentage of each group of PAHs retained in solution vs. final volume, after the concentration of a concentrated solution (starting conc.=0.167 μg/mL) from a 300-mL to the desired volume (1, 3, 5, 30, 50 mL)

divided all 16 PAHs into 2-, 3-, 4-, 5-, 6-ring PAH and total-PAH groups. Correspondingly, the average recoveries of each group were 77.5 ± 5.0, 80.1 ± 6.2, 83.5 ± 4.3, 84.3 ± 2.8, 84.8 ± 2.4, and 82.5 ± 4.3%, respectively (Figure 4). Obviously, large losses occurred when the concentrated solutions of PAH were evaporated to 1 mL. As for evaporating the concentrated solutions to 3 mL, only naphthalene (2-ring PAH, 87.4 ± 3.5%), acenaphthylene (3-ring PAH, 88.1 ± 3.4%) and acenaphthene (3-ring PAH, 88.3 ± 3.6%) had the percent recoveries below 90.0%, while the other 13 PAHs were all above. For individual compounds, the corresponding standard deviations of the percent recoveries ranged from 1.8 to 4.6% with a mean value of 3.0%. The recoveries seemed to be quantitative for most PAH compounds when the concentrated solutions were evaporated to 3 mL. As for concentrated solutions evaporated to 5, 30, and 50 mL the analytes recovered were all greater than 90.0% (92.5~98.0%) and the corresponding standard deviations were between 1.6% and 7.3%. In other words, evaporating the concentrated PAH solution (0.167 μg/mL) with nitrogen gave acceptable recoveries if evaporation stopped at a final volume of 3~5 mL, which meant a concentration factor between 60 and 100. But when the concentrated solutions were reduced to below 3~5 mL, analyte recovery provided poor recoveries.

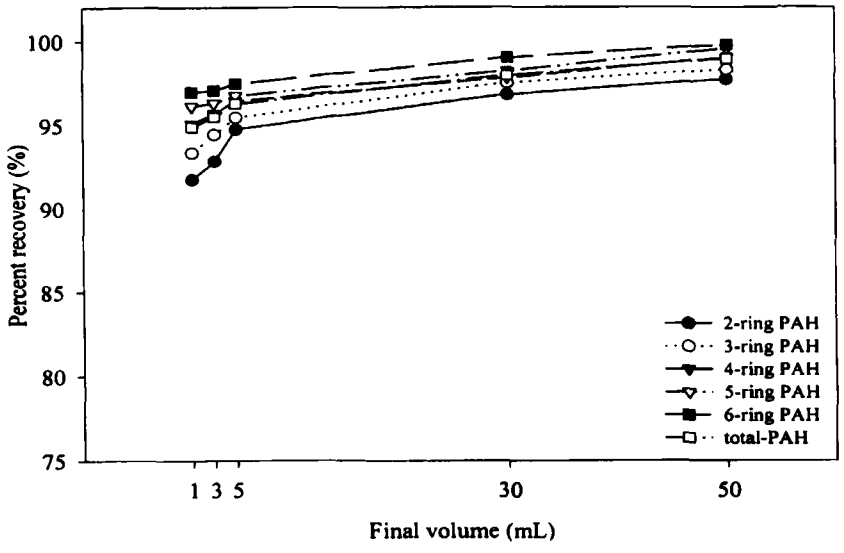

FIGURE 5 Percentage of each group of PAHs retained in solution vs. final volume, after the concentration of a diluted solution (starting conc.=0.00333 μg/mL) from a 300mL to the desired volume (1, 3, 5, 30, 50 mL)

After evaporating the diluted solutions (starting concentration = 0.00333 μg/mL) to 1 mL, shown in Figures 3 and 5, percent recoveries (± standard deviation) were found all above 90.0% (91.5~97.6% ± 1.0~6.0%). Better recoveries were observed when the PAH solutions were concentrated to 3 mL (92.9~99.2% ± 2.1~4.9%). When the diluted solutions were concentrated to 5, 30 and 50 mL, all compounds had percent recoveries (± standard deviation) above 94.0% (94.4~100.7% ± 1.5~8.3%). Unlike the concentrated solution, concentrating the diluted PAH solution (0.00333 μg/mL) to 1 mL with nitrogen evaporation provided very good recoveries.

Figures 4 and 5 show that for all groups of PAH studied, for both concentrated and diluted solutions, no significant difference was found between their recoveries when the PAH solutions were concentrated to 5 mL. However, when further concentrated, the difference between different groups of PAHs began to increase slightly with the decreasing final volume. Discrimination was nearly unnoticeable among different groups of PAHs. In addition, losses increased exponentially with respect to the final volume. More importantly, not only did they decrease with respect to the smaller final volume, but also decreased more rapidly than volumes above 5 mL.

A conclusion reported by Ferreira et al.[12] helps to explain why the analyte losses were dependent on the final volume reached. In that study, Ferreira et al. proposed that analyte losses should be proportional to the wet surface area / remaining liquid volume ratio. But Ferreira's study used a K-D concentrator while this study used a nitrogen stream. The K-D concentrator works like a distillation system where droplets from the splash make most of the area near the surface of the solution wet. On the other hand, the nitrogen evaporation works like a purging system, causing a violent gas stream, forming no observable splashes and consequently, wetting a much smaller surface area (or dries the wetted surface area rapidly).

Still Ferreira's conclusion is applicable to this study, but in order to account for the different conditions in the evaporative glass flask we changed the coefficient of Ferreira's conclusion, namely, the function of wet surface area. Accordingly, it is plausible that the analytes losses increase exponentially with respect to the final volume reached, as represented in Figures 4 through 6.

Study of the influence of the starting sample concentration

Figure 6 shows that analyte losses increase drastically as the volume drops below 5 mL. In Figure 6, each curve is a function of the starting sample concentration and practically independent of the boiling points of the analytes. Our observations show the higher the starting sample concentration, the more the analytes lost. Also, analyte losses occurred much faster when the solution was concentrated down to below 5 mL. Surprisingly, this conclusion seems to contradict those reported by other researchers.[12,16]

Grob and Müller[16] evaporated two sets of test mixtures (a standard solution, a solution of 20 times standard) with a stream of nitrogen from 800 μL to dryness, then, re-diluted them to 200 μL for the subsequent GC analysis and concluded that the more concentrated the solution the higher the recovery. Ferreira et al.[12] also conducted concentration experiments with a micro-Kuderna-Danish concentrator and obtained the same conclusion. Let us carefully inspect the point of view of each study in order to explain this contradiction.

Ferreira et al.[12] adopted a concept advanced by Grob, Jr. and Bossart,[17] and Ferreira et al.[18] This concept states that the presence of less volatile material can change the sample evaporation behavior, prolonging the lifetime of the solvent droplets that evaporate around a nucleus made of less volatile material. Therefore, during the K-D concentration procedure some of these solutes may play a similar role with the less volatile material. When the concentration begins the solvent droplets, coming from splashes or re-condensation, adhere to the less volatile solutes and are deposited on the glass wall. The droplets take longer to

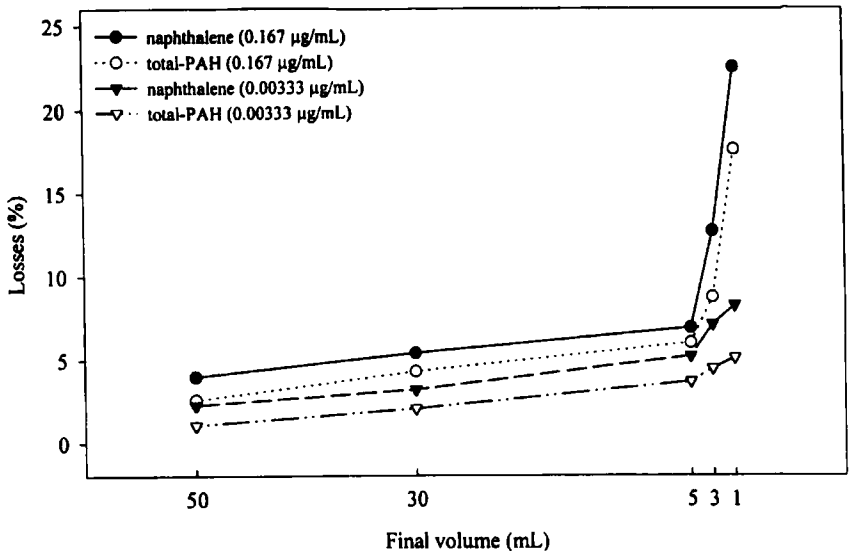

FIGURE 6 Analyte losses through the sample concentration procedure are a function of both final volume reached and starting sample concentration

evaporate, thus delaying the release of solutes contained in them and lowering the amount of solute lost during this step. Once the majority of the solvent that forms the droplet has evaporated, the thickness of the solute coating covering the glass wall makes the retention capacity of the more concentrated solution temporarily larger while avoiding solute loss or at least, delaying its release. That is the explanation of Ferreira et al.[12] on why the more concentrated solutions have higher recoveries than those in the diluted ones.

The contradictory conclusions, proposed in Ferreira et al.,[12] are a direct result of using the K-D concentration method. In a K-D concentrator, coevaporation is the main mechanism of solute loss for analytes with high boiling points. Accordingly, a diluted solution is more influenced by coevaporation than concentrated solutions in a K-D concentration system. But in our study, under a violent gas stream (as described in previous section) the solvent vapors are promptly carried out of the flask and the wetted surface of the flask is dried quickly. Therefore, the extent of coevaporation for the diluted solutions is not likely to be more significant than that of the concentrated solutions.

As for Grob and Müller,[16] they consider that: (1) the losses are drastically increased for both concentrated and diluted if the solutions are evaporated to dryness, (2) the thinner the layer of solute material, the higher is the vapor pressure

of deposited materials (the retention power of thin film is small), and (3) the losses decrease when the solute concentration is increased because the thickness of the solute material on the glass wall is determined by this factor. Most importantly, they also point out that solvent evaporation under a stream of nitrogen caused relatively small amounts of solute material to co-evaporate as long as there remained some condensed solvent. Also, the loss was less when compared to evaporating to dryness.[16] In other words, they found that most of the solute was lost when dryness was reached and that a diluted solution lost more easily than a concentrated one. But unfortunately and unlike our study, they did not give powerful evidence about losses caused by nitrogen evaporation to a desired volume (before dryness).

Grob and Müller[16] evaporate the solution until dryness, while our study was only to 1 mL. Grob and Müller[16] point out that there is relatively little solute material lost as long as some solvent remained. But when evaporated to dryness significant losses of solute occurred especially in diluted solutions. It can be assumed that up until the point of before dryness the solute loss shows similar results to our research. Also, the contradictory evidence is due to that very large proportions of analytes are lost when solutions are evaporated to dryness, especially for the diluted solutions. So measuring at dryness rather than before dryness significantly influenced analyte recovery.

Lastly, Grob and Müller[16] suggest the thicker the film, the greater the retention power of solute material. Concentrated solution should provide thicker film than that of diluted solution. Therefore, the loss of analytes should naturally be greater in diluted solution rather than that of concentrated. But in fact, the opposite does occur in our study. Concentrated solutions deposit thicker film on the glass wall but because of this thickness, the aggressive nature of a nitrogen stream actually blows more solute material away than if the deposit was thinner. Thus, because the analytes of concentrated solutions are more readily deposited on the surface of the glass and the nature of the nitrogen stream, the loss of analytes in these solutions is larger.

CONCLUSIONS

In this study, the amount of PAH lost during the concentration procedure depended on three factors: the boiling point of the compound (slight affect), the final volume reached (significant affect) and the starting sample concentration (significant affect). Evaporation with a stream of nitrogen is a very efficient procedure for concentrating PAH solutions down to about 3~5 mL, which means a

concentration factor between 60 and 100. For a diluted solution, nitrogen evaporation to a final volume of 1 mL appears to provide PAHs with a qualitative and quantitative solute recovery. Notice that for concentrated solutions evaporated to a volume less than 1 mL with a stream of nitrogen, resulted in large solute losses (e.g., more than 22.5% for naphthalene). But for practical measures, concentrated solutions do not need further concentration because of the simple fact that they are already highly concentrated. Therefore, special precautions are needed at this stage: concentrating a PAH solution to a final volume below 1 mL or to dryness should be avoided.

Large-volume-injection (LVI) technique may be a reasonable alternative if a solution, containing very trace amounts of PAH, needs to be concentrated to a final volume below 1 mL. However, obtaining more reproducible results is a problem for LVI technique.

Further studies on other factors (solvent type, smaller final volume, geometry of flask, purging flow rate, temperature, etc.) affecting solute losses using a nitrogen concentration system as well as a comparison of the characteristics of solute losses caused by various concentration systems are both suggested.

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