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High-precision sampling of sub-nanogram, low-parts-per-billion solutes from liquids using the dynamic solvent effect

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ABSTRACT

The quantitative precision of dynamic solvent-effect sampling from solvent specimens is reported. For sub-nanogram amounts of a range of solutes at a concentration of $5{:}10^9$ the coefficients of variation of peak areas, peak percentage areas and peak-area ratios are consistently below 10%. The dynamic solvent effect allows high-precision sampling of much smaller amounts of solute than do alternative sampling methods.

INTRODUCTION

The dynamic solvent effect is a sampling technique for capillary gas–liquid chromatography which exploits the peculiar chromatographic properties of evaporating solvent films to accumulate quantitatively trace components from either liquid or gaseous specimens. During sampling volatiles are accumulated at the evaporating, upstream edge of a film of solvent held in dynamic equilibrium between evaporation and capillary rise in an axially perforated porous bed[1,2].

The dynamic solvent effect was developed to allow the quantitative analytical capability of the capillary column and its associated detectors to be fully realized for specimens where great dilution or restricted availability limit the total amount of each solute to a few nanograms. Such specimens are most commonly encountered in work on biological[3] or clinical problems.

Dynamic solvent-effect sampling can be applied to either liquid or gaseous specimens. Its quantitative performance with liquid specimens is reported here.

EXPERIMENTAL

Separations were carried out on a Varian 3700 gas chromatograph fitted with a dynamic solvent-effect inlet[2]. The column, produced in-house, was 25 m × 0.3 mm I.D. borosilicate glass, coated with 0.4 μm of methylsilicone. The initial temperature of

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the inlet and column was 40°C, the inlet was ballistically heated to 220°C after 4 min or 3.5 min, depending on the solvent evaporation time of the concentrator, and the column temperature was programmed at 10°C min^{-1} to 250°C after 7 min, or at 5°C min^{-1} for the Grob mixture[4]. The carrier gas was hydrogen with a linear velocity of 50 cm s^{-1}. Flame ionization detection was used at a sensitivity of 10^{-11} A mV^{-1} and chromatograms were recorded on a Varian 4270 integrator with a full-scale deflection of 2 mV.

The system's qualitative performance was tested by sampling 100 μl of Grob mixture at a concentration of 1:10^8 (*ca.* 1 ng per peak) and 130 μl of a diagnostic test mixture for solvent-effect inlets[5] at a concentration of 5:10^9 (*ca.* 0.65 ng per peak).

The quantitative precision of dynamic solvent-effect sampling from a solvent matrix was tested by running five consecutive samples of the diagnostic test mixture on each of three dynamic solvent-effect concentrators. Pilot studies had already established that errors due to adsorption on containers and volumetric glassware exceeded those due to sampling by the dynamic solvent effect[6], so sampling was consequently carried out directly from a 10-cm^3 stock specimen of test mixture without measuring into other containers. The concentration of the test mixture was 5:10^9. Each sample was obtained by passing 10 cm^3 min^{-1} of palladium-cell-purified hydrogen through a dynamic solvent-effect concentrator dipped into the bulk specimen at 29.6°C. From calibrations of the detector response, based on split injections, *ca.* 0.65 ng of each component was present in each sample, which agreed with the consumption of solution for each sample, determined gravimetrically to be 130 μl.

Standard deviations of peak areas and peak percentage areas (the percentage of the sum of the solute peak areas contributed by a particular peak) were calculated from integrator reports from five consecutive runs, the relative standard deviation being the standard deviation divided by the mean, expressed as a percentage. Standard deviations and relative standard deviations were also calculated for the ratios of areas between pairs of peaks.

The linearity of peak area *vs.* specimen concentration was tested by sampling a series of progressively more dilute test mixture solutions on one concentrator. A 5-cm^3 volume of test mixture at a concentration of 2:10^7 was prepared in *n*-hexane. For each specimen *ca.* 0.5 cm^3 of solution was decanted into a holder that had been rinsed with the same solution to reduce its adsorptive activity. Each specimen was sampled for 10 min (130 μl) with a 10 cm^3 min^{-1} flow of palladium-cell-purified hydrogen at 29.6°C. The residue of the test mixture was then diluted to approximately the original volume with *n*-hexane, and another specimen was sampled and run. To minimize exposure of the test mixture to adsorptive glass surfaces, the amounts of solution and of added hexane at each stage were determined gravimetrically rather than volumetrically. This process was repeated until the smallest chromatographic peaks were *ca.* 200 counts in area (*ca.* 0.065 ng). Peak areas were plotted against calculated concentrations and the straight line giving the best, least-squares fit was calculated.

RESULTS

Except for slight adsorptive activity towards the alcohols of the two test mixtures and the strong base of the Grob mixture, the system was extremely inert (Figs. 1 and 2).

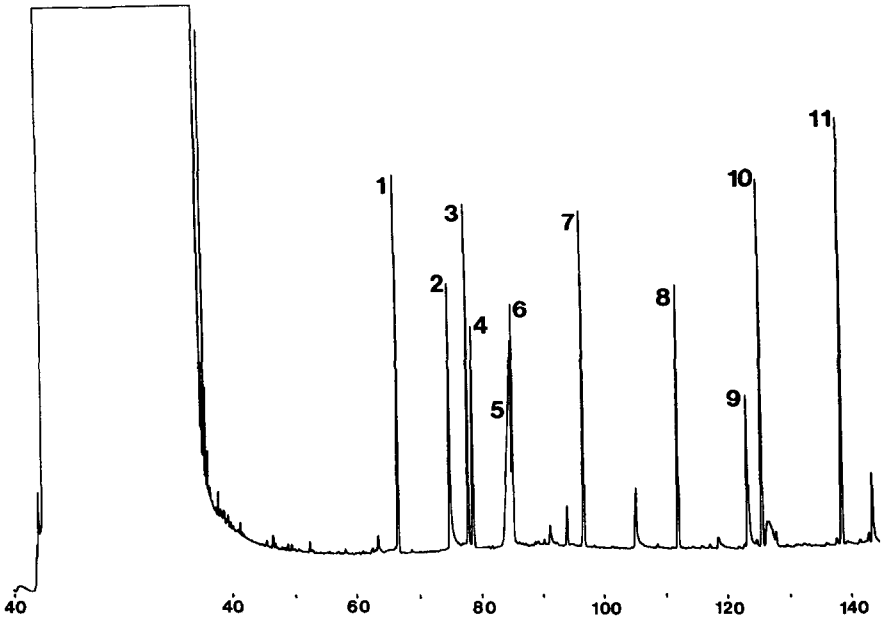

Fig. 1. Chromatogram from 100 μl of 1:10^8 Grob mixture (*ca.* 1 ng per peak) sampled by the dynamic solvent effect and separated on a 25 m × 0.3 mm I.D. methylsilicone (0.4 μm) column. For analytical conditions, see text. Peaks: 1, *n*-decane; 2, *n*-octanol; 3, *n*-nonanal; 4, 2,6-dimethylphenol; 5, ethylhexanoic acid; 6, 2,6-dimethylaniline; 7, *n*-dodecane; 8, methyl decanoate; 9, dicyclohexylamine; 10, methyl undecanoate; 11, methyl dodecanoate. The abscissa is temperature (°C).

Despite the small amounts and dilute solutions involved, dynamic solvent-effect sampling achieved high precisions of peak areas, peak percentage areas and peak-area ratios for all components of the diagnostic test mixture. Except for the dimethylaniline peak, the relative standard deviations of the peak areas and percentage areas were always below 10% even when the results from the three concentrators were pooled. The relative standard deviations of the peak-area ratios were all below 10% (Tables I–VI).

For amounts per peak ranging from *ca.* $6 \cdot 10^{-11}$ g to $2.3 \cdot 10^{-8}$ g, over three orders of magnitude of specimen concentration, the relationship of peak area to specimen concentration was perfectly linear for all except the dimethylaniline and *n*-decanol peaks (Table VII).

DISCUSSION

The results presented here confirm those obtained earlier[6] with 2–3 ng per component at specimen concentrations of 1:10^8.

The external standard method of quantification involves dividing the area of an experimental peak by the area of a peak obtained from an independently determined amount of the same compound[7]. Therefore, the variance of the calculated mass will be the sum of the variances of the peak area and of the estimate of the standard amount.

TABLE I

RELATIVE STANDARD DEVIATIONS OF PEAK AREAS AND PEAK PERCENTAGE AREAS FOR DYNAMIC SOLVENT-EFFECT SAMPLING OF 130 µl FROM A BULK 5:10^9 TEST MIXTURE IN *n*-HEXANE

$n = 5$ on each of three concentrators. Approximately 0.65 ng per compound.

Compound	*Relative standard deviation (%)*					
	Concentrator 1		*Concentrator 2*		*Concentrator 3*	
	Area	*% area*	*Area*	*% area*	*Area*	*% area*
n-Octane	1.46	1.27	2.70	2.33	2.86	0.87
n-Nonane	1.05	0.33	1.03	0.99	3.38	0.42
2,6-Dimethyl-4-heptanone	0.98	1.46	1.22	0.95	3.75	0.49
n-Decane	1.40	0.75	1.34	0.78	3.43	0.25
p-Cresol	2.75	1.85	0.47	1.87	3.56	0.57
Linalool	1.63	1.01	2.21	1.06	2.84	1.25
Dimethylaniline	2.54	1.90	2.72	2.69	6.12	5.45
n-Dodecane	0.60	0.58	2.47	1.06	3.57	0.26
n-Decanol	1.91	2.74	1.56	0.81	4.87	2.12
Methyl decanoate	0.69	0.39	2.38	1.90	4.11	0.67
n-Tetradecane	0.60	0.58	3.92	2.60	3.96	0.83
n-Pentadecane	1.17	0.81	4.56	3.99	3.48	0.78

TABLE II

COMPARISON OF MEAN PEAK AREAS OF EACH COMPONENT OF A 5:10^9 SOLVENT-MATRIX TEST MIXTURE SAMPLED FROM THE BULK ON EACH OF THREE DYNAMIC SOLVENT-EFFECT CONCENTRATORS AND OVERALL RELATIVE STANDARD DEVIATIONS (R.S.D.) OF PEAK AREAS FROM FIVE SAMPLES ON EACH OF THREE CONCENTRATORS

Compound	*Mean peak area ($n = 5$)*			*R.S.D. (%)*
	Concentrator 1	*Concentrator 2*	*Concentrator 3*	
n-Octane	3011	2811	2806	4.08
n-Nonane	3044	2786	2617	6.71
2,6-Dimethyl-4-heptanone	3116	2844	2645	7.25
n-Decane	2798	2530	2395	7.03
p-Cresol	3626	3045	3046	9.02
Linalool	2685	2466	2298	6.99
Dimethylaniline	3287	3005	2176	17.61
n-Dodecane	2851	2531	2386	8.07
n-Decanol	3013	2648	2758	6.33
Methyl decanoate	4388	3877	3592	8.96
n-Tetradecane	3265	2879	2651	9.39
n-Pentadecane	4288	3820	3511	9.05

TABLE III

AS TABLE II FOR MEAN PERCENTAGE PEAK AREAS

Compound	*Mean peak % area (n = 5)*			*R.S.D. (%)*
	Concentrator 1	*Concentrator 2*	*Concentrator 3*	
n-Octane	8.057	7.985	8.576	4.96
n-Nonane	7.867	7.904	7.966	1.44
2,6-Dimethyl-4-heptanone	8.009	8.069	8.046	1.07
n-Decane	7.190	7.179	7.286	1.22
p-Cresol	9.047	8.699	9.233	3.16
Linalool	6.917	6.941	6.991	1.49
Dimethylaniline	7.832	8.526	6.622	11.77
n-Dodecane	7.227	7.182	7.259	0.81
n-Decanol	7.852	7.514	8.389	5.41
Methyl decanoate	11.023	10.999	10.924	1.07
n-Tetradecane	8.173	8.165	8.063	1.91
n-Pentadecane	10.804	10.838	10.683	2.38

Internal standardization involves comparison of the areas of two peaks on the same chromatogram[8]; in this instance the relative standard deviations of peak-area ratios (Tables IV–VI) provide a direct measure of the highest available precision. If the dynamic solvent effect is used for sampling, the precision of both techniques will probably be limited by the variance of the estimate of the standard amounts rather than by sampling variations. A good linearity of peak area *vs.* concentration (Table VII) is desirable for both internal and external standardization.

The high precision of the peak-area ratios (Tables IV–VI), even between sub-nanogram amounts of compounds of different chemical character, is a feature of

TABLE IV

RELATIVE STANDARD DEVIATIONS (%) OF PEAK-AREA RATIOS FOR 130 µl OF 5:10[9] TEST MIXTURE SAMPLED BY THE DYNAMIC SOLVENT EFFECT USING CONCENTRATOR 1

Abbreviations in the column headings correspond to the compounds in the first column.

Peaks	C_8	C_9	*8-one*	C_{10}	*pCr*	*Lin*	*DMA*	C_{12}	*10-ol*	*Me-10*	C_{14}	C_{15}
n-Octane	–	1.27	1.41	1.98	2.49	2.03	1.54	1.19	2.91	1.51	1.59	1.91
n-Nonane			0.26	0.88	1.77	1.20	1.94	0.56	2.96	0.59	0.68	0.71
2,6-Dimethyl-4-heptanone				0.70	1.85	1.02	2.01	0.63	2.87	0.49	0.61	0.69
n-Decane					1.67	0.53	2.20	1.24	3.08	0.78	0.95	0.90
p-Cresol						1.82	2.03	2.28	4.55	2.11	2.26	1.93
Linalool							1.98	1.56	3.19	1.12	1.33	1.41
Dimethylaniline								2.24	4.10	2.27	2.46	2.57
n-Dodecane									2.47	0.54	0.48	0.84
n-Decanol										2.47	2.38	2.94
Methyl decanoate											0.24	0.69
n-Tetradecane												0.62
n-Pentadecane												–

TABLE V

AS TABLE IV, USING CONCENTRATOR 2

Peaks	C_8	C_9	*8-one*	C_{10}	*pCr*	*Lin*	*DMA*	C_{12}	*10-ol*	*Me-10*	C_{14}	C_{15}
n-Octane	–	1.99	1.73	2.09	2.09	2.72	3.65	2.54	3.09	2.78	3.93	5.54
n-Nonane			0.31	0.42	0.97	1.14	2.34	1.63	1.44	1.67	3.53	4.62
2,6-Dimethyl-4-heptanone				0.50	1.04	1.47	2.57	1.58	1.51	1.64	3.38	4.58
n-Decane					1.24	1.03	2.22	1.22	1.30	1.29	3.32	4.59
p-Cresol						2.10	2.65	2.38	2.19	2.46	4.28	5.28
Linalool							2.20	0.52	1.40	0.60	3.02	4.61
Dimethylaniline								2.46	2.83	2.64	4.93	6.01
n-Dodecane									1.57	0.45	2.73	4.53
n-Decanol										1.24	2.64	3.48
Methyl decanoate											2.45	4.14
n-Tetradecane												2.58
n-Pentadecane												–

dynamic solvent-effect sampling that has already proved to be valuable in the field of semiochemistry, where the biological properties of a mixture of volatiles depend on their relative concentrations[2].

The literature was surveyed for data on the quantitative performance of sampling systems designed to handle specimens similar to those used here. Disappointingly, quantitative precision is not an aspect of analytical performance that has received general attention[9]. Indeed, it was the exception, rather than the rule, that this type of data accompanied, or even followed, descriptions of sampling techniques. Even among those papers where precision was reported, its interpretation was confounded by a lack of information on the composition of the test specimens employed[10–14]. Studies for which test mixture composition and concentration were reported are presented in Table VIII.

A comparison of the data for the dynamic solvent effect in Tables I–VI with those from other systems in Table VIII reveals that the dynamic solvent effect yields

TABLE VI

AS TABLE IV, USING CONCENTRATOR 3

Peaks	C_8	C_9	*8-one*	C_{10}	*pCr*	*Lin*	*DMA*	C_{12}	*10-ol*	*Me-10*	C_{14}	C_{15}
n-Octane	–	0.98	1.26	1.24	1.14	1.83	6.07	1.15	2.38	1.64	1.71	1.06
n-Nonane			0.33	0.37	0.44	1.43	5.67	0.36	2.01	0.74	1.08	0.80
2,6-Dimethyl-4-heptanone				0.45	0.48	1.59	5.69	0.41	1.91	0.49	1.05	0.95
n-Decane					0.57	1.15	5.35	0.38	2.22	0.76	1.06	0.97
p-Cresol						1.57	5.87	0.64	1.74	0.64	0.98	0.84
Linalool							4.51	1.43	3.26	1.84	1.87	1.81
Dimethylaniline								5.57	7.40	5.82	5.81	6.05
n-Dodecane									2.05	0.65	0.86	0.72
n-Decanol										1.66	1.69	1.74
Methyl decanoate											0.79	1.00
n-Tetradecane												0.68
n-Pentadecane												–

TABLE VII

COEFFICIENTS OF DETERMINATION (r^2) OF THE LINES OF BEST LEAST-SQUARES FIT FOR PEAK AREA *VS.* SPECIMEN CONCENTRATION WHEN TEST MIXTURES WITH CONCENTRATIONS BETWEEN $2{:}10^7$ AND $2.8{:}10^{10}$ WERE SAMPLED BY THE DYNAMIC SOLVENT EFFECT

Compound	r^2	*Compound*	r^2
n-Octane	1.000	2,6-Dimethylaniline	0.999
n-Nonane	1.000	*n*-Dodecane	1.000
2,6-Dimethyl-4-heptanone	1.000	*n*-Decanol	0.995
n-Decane	1.000	Methyl decanoate	1.000
p-Cresol	1.000	*n*-Tetradecane	1.000
Linalool	1.000	*n*-Pentadecane	1.000

a precision at least as high as that provided by other sampling methods. The marked superiority of the dynamic solvent effect lies in its ability to generate such precision with amounts of test solute up to three orders of magnitude smaller than those employed elsewhere, with dilutions up to seven orders of magnitude greater, and with a wide range of test solutes considerably less chromatographically tractable than the hydrocarbons and halocarbons more commonly employed. The only work involving

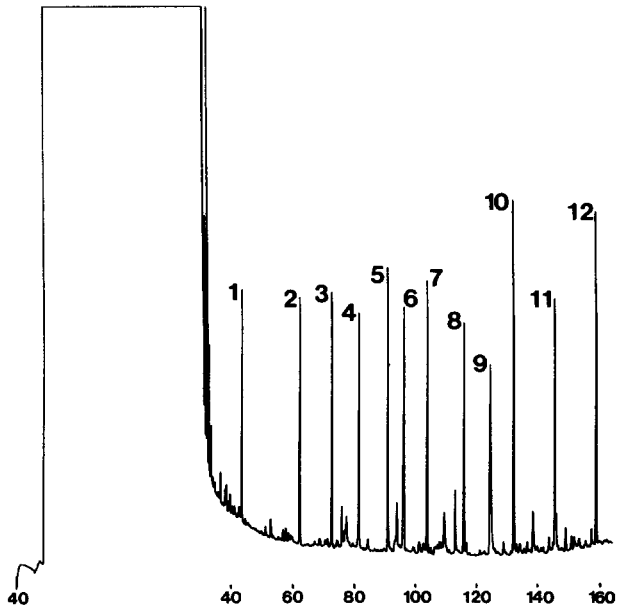

Fig. 2. Chromatogram from 130 μl of $5{:}10^9$ diagnostic test mixture (*ca.* 0.65 ng per peak) sampled by the dynamic solvent effect and separated on a 25 m × 0.3 mm I.D. methylsilicone (0.4 μm) column. For analytical conditions, see text. Peaks: 1, *n*-octane; 2, *n*-nonane; 3, 2,6-dimethyl-4-heptanone; 4, *n*-decane; 5, *p*-cresol; 6, linalool; 7, 2,6-dimethylaniline; 8, *n*-dodecane; 9, *n*-decanol; 10, methyl decanoate; 11, *n*-tetradecane; 12, *n*-pentadecane. The abscissa is temperature (°C).

TABLE VIII

QUANTITATIVE PERFORMANCE OF A VARIETY OF SAMPLING METHODS FOR THE GAS CHROMATOGRAPHIC DETERMINATION OF TRACE COMPONENTS IN SOLVENTS

Techniques are abbreviated as follows: ads = adsorption; ct = cold trapping; ECD = electron-capture detection; FID = flame ionization detection; MS = mass spectrometric detection; NPD = nitrogen–phosphorus detection; oc = on-column injection; ptv = programmed-temperature vaporizer; sl = splitless injection; sp = splitting; TIM = total ion monitoring; vi = valve inlet.

Solutes[a]	*Technique*	*Concentration or mass*	*R.S.D. (%)*	*Ref.*
Alkanes	ptv, FID	10%	0.2–14	16
C_{18}–C_{32} alkanes	ptv, FID	250 ng : 20 μl	0.9–5.2	17
Cl compounds	ptv, ECD	1 ng : 1 μl	2.4–7.0	17
P pesticides	ptv, NPD	1 ng : 5 μl	1.0–2.1	17
Mixed	9c, sl, FID	10–40 ng : 1 μl	0.5–4.2	18
Halocarbons	ads, ct, TIM	200 ng : 1 μl	3–44.4	19
Varian mix	vi, oc, FID	400 ng : 1 μl	0.05–1.9	20
C_8–C_{10} alkanes	vi, ct, sp, FID	500 ng : 0.5 μl	3–6	21
C_{10}–C_{28} alkanes	ptv, FID	240 ng : 0.2 μl	0.7–5.7	22
C_{10}–C_{18} alkanes	oc, FID	44 ng : 0.4 μl	0.5–1.2	23
Alkanes	sp, FID	160–1600 ng	1.7–33.1	24
Alkanes	sp, ptv, FID	160–1600 ng	0.9–6.23	24
Cl pesticides	vi, ECD	16 ppt	4.4	15
Cl pesticides	vi, ECD	40 ppt	2.2–9.5	16
PCBs, PBBs	ads, ct, TIM	75 ng : 100 μl	10–19	25
C_{10}–C_{32} alkanes	oc/sl, FID	0.002%	2–3.1	26
C_{10}–C_{32} alkanes	sp, FID	0.1%	1.5	26
PAHs	ads, ct, FID	0.4–1 μg : 100 μl	1.2 ± 0.6	27
n-Eicosane	oc, FID	15 ng : 1 μl	1.6–4.8	28
C_9–C_{36} alkanes	oc, FID	3.6–10.3%	0.4–9.4	29
Phenols, PAHs	sp, MS	30 ng : 1 μl	13–41	30
C_{18}–C_{32} alkanes	sp/sl, FID	250 ng : 20 μl	0.8–5.2	31
C_{10}–C_{32}	sl/oc, FID	2 : 10^5, 0.2–0.5 μl	0.1–1.5	32
Alkanes	ptv, FID	100 ng : 2 μl	0.5–17.8	33
Ethyl esters	ptv, FID	100 ng : 2 μl	0.8–46.6	33
n-Alcohols	ptv, FID	100 ng : 2 μl	0.5–24.0	33
Carboxylic acids	ptv, FID	100 ng : 2 μl	0.5–19.9	33

[a] PCBs = Polychlorinated biphenyls; PBBs = polybrominated biphenyls; PAHs = polynuclear aromatic hydrocarbons.

comparable specimen volumes and smaller amounts of solute was that by Zlatkis *et al.*[15] in which the specific and highly sensitive electron-capture detector was used.

The linearity of peak area *vs.* specimen concentration for dynamic solvent-effect sampling matches or exceeds that of any other system and should prove adequate for all applied work.

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