QUANTITATIVE PURGEABILITY OF ORGANICS FROM WATER AND ITS APPLICATIONS

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Environmental and workplace requirements for water sampling and analysis of organic compounds are increasing. A very simple and sensitive method for such analyses is the purge-and-trap procedure developed by the Environmental Protection Agency and used mostly for trihalomethanes and other halocarbons.[1,2] In considering the use of this technique for the analysis of water samples, researchers in HSE-9 investigated whether acetone, ethyl propionate, and toluene could be quantitatively purged, trapped, desorbed, and analyzed by gas chromatography. Without guidelines to answer this question, the Environmental Chemistry Group attempted the analysis with success.

During these analyses, some of the water standards containing these three compounds were purged several times with 180 mL helium rather than purged the usual one time. The subsequent purgings produced nearly the same amount of acetone, less ethyl propionate, and no toluene compared with the first purging. The purgeability was obviously not an increasing function of volatility (boiling points of 56.5°C, 99°C, and 110.6°C, respectively) but apparently was a decreasing function of solubility (miscible, 1.7% soluble, and very slightly soluble, respectively). These observations raised the question whether a quantitative definition of purgeability would have any usefulness for water analyses.

Bellar and Lichtenberg[1] briefly studied the purging of methylene chloride, chloroform, benzene, 2-butanone, and eight hydrocarbons. The authors concluded that water-insoluble (<2% soluble) compounds can be purged from 5 mL of water by using 150 mL of nitrogen, but water-soluble materials whose partition coefficients do not favor the gaseous phase are only qualitatively transferred regardless of the purge volume. This result implied that the purge-and-trap technique was useless for the more soluble compounds, which is contrary to our successful analysis of acetone. Therefore, the matter was studied further.

The experimental plan was to purge prepared solutions of selected organics in water a number of times and to observe the relative amounts removed during each purge. The apparatus used were a Valco Instruments Company trace organics concentrator (purge/trap), a Perkin Elmer Model 900 gas chromatograph (GC) with flame ionization detector, and a Hewlett Packard Model 3390A integrator. Five-milliliter samples of water were purged at 2°C with helium for 6 min at 30 mL/min. Samples collected on the Tenax column were desorbed at 180 or 200°C for 9 min with the helium carrier flow (15-35 mL/min) into the GC. The analytical GC column was Porapak QS (50/80 mesh in 1.8-m-long × 3.2-mm-o.d. stainless steel) operated at 200 or 220°C.

Two classes of compounds—alcohols and ketones—were studied at the initial concentrations shown in Table XVI. The results are shown in Fig. 6 as plots of log (relative peak area) versus number of times purged. These plots are linear with negative slopes (Table XVI) increasing within each class with increasing molecular weights. The slopes for ketones were much greater than those for alcohols, even with the same molecular weight and elemental composition (for example, acetone versus n-propanol).

TABLE XVI. Purgeabilities of Selected Alcohols and Ketones

Compound	Solubility in Water (%)	Boiling Point (C°)	Initial Concentration (g/L)	Purgeability[a] (Fraction/Purge)	Std Dev
Methanol	M[b]	64.7	0.30	0.0085	0.0001
			0.18	0.0094	0.0017
Ethanol	M	78.5	0.18	0.0100	0.0008
1-Propanol	M	97.2	0.19	0.0148	0.0006
1-Butanol	9.1	117.5	0.019	0.0288	0.0029
1-Octanol	0.06	194.5	0.019	0.3366	0.0171
Acetone	M	56.5	0.054	0.0651	0.0011
			0.036	0.0743	0.0012
			0.036	0.0624	0.0052
2-Butanone	27.5	79.5	0.31	0.1332	0.0013
4-Methyl-2-pentanone	1.9	117.5	0.31	0.3596	0.0088
2,4 Pentanedione	12.5	140.5	0.045	0.0328	0.0028

[a]Defined as the slopes of plots such as Fig. 6.
[b]Miscible with water in all proportions.

The linear relationships shown in Fig. 6 imply that a constant fraction of the sample in water is purged each time, regardless of the amount present. The establishment of equilibrium with a constant partition coefficient between water and the helium flowing through it would account for this.

Purgeability can be defined quantitatively as the slope of a plot, as in Fig. 6, with appropriate units of purge gas volume and type (i.e., fraction/milliliter helium). This purgeability is apparently much more a function of solubility than of volatility (Table XVI). The lower-boiling organic compounds in a class are typically also more soluble in water and therefore less completely purged. The limitation suggested by Bellar and Lichtenberg[1] of 2% solubility is apparently not valid, because even the water-miscible alcohols were successfully purged and

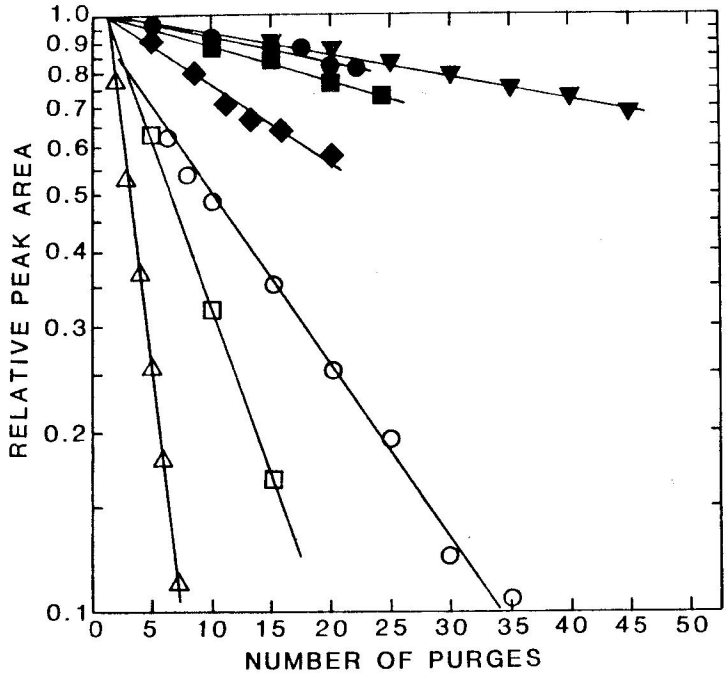

FIGURE 6
Typical plots of relative gas chromatographic peak areas versus number of purges of a water sample: ▼ methanol; ● ethanol, ■ 1-propanol; ♦ 1-butanol; O acetone; □ 2-butanone (methyl ethyl ketone); △ 4-methyl-2-pentanone (methyl isobutyl ketone).

analyzed. However, because only small fractions of the very solubles are purged each time, their detection limits are raised correspondingly. An advantage of analyzing the very solubles is that repetitive purges of the same sample are possible, giving better statistics (extrapolation to an initial value) and not requiring as much total water sample.

Applications of repetitive purge/trap analysis include

1. Identifying unknowns in a water sample by quantitatively determining the purgeability factor. Gas chromatographic peak retention times alone are not sufficient to identify compounds. At least one other characteristic must be determined (mass spectrum, retention time on another column, infrared spectrum, etc.). Purgeability is readily determined in a purge-and-trap GC analysis and, with very little extra effort and no additional equipment, provides another quantitative parameter with which to identify unknowns in a sample.
2. Separating the contributions of coeluting compounds (indistinguishable retention times).
3. Cleaning complicated chromatograms as the less soluble compounds are removed and reduced.
4. Identifying hydrolysis or other reactions occurring in water solutions. This situation is more likely with freshly prepared standards and quality control samples. Actual samples are usually at equilibrium. If such reactions are occurring, serious calibration errors could result from using fresh nonequilibrated standards.

Some of these applications are illustrated in Fig. 7. A water solution containing 2,4-propanedione (acetylacetone) was purged seven times, giving the gas chromatograms shown. The first large peak at the retention time of acetone (10.35 min) was much smaller on the second purge, showing that the peak was not all acetone. On subsequent purging, the peak areas dropped with a slope characteristic of acetone. This slope could be extrapolated to give the actual initial acetone concentration without the contribution of the unknown coeluting peak. From its high purgeability, this unknown is relatively insoluble; from its short gas chromatographic retention time, it is relatively volatile. Together, these two clues limit the possibilities for this unknown impurity or decomposition product in the 2,4-propanedione used. From the purgeability, we could determine that the second major peak (at 15.90 min), not the first, was due to 2,4-pentanedione.

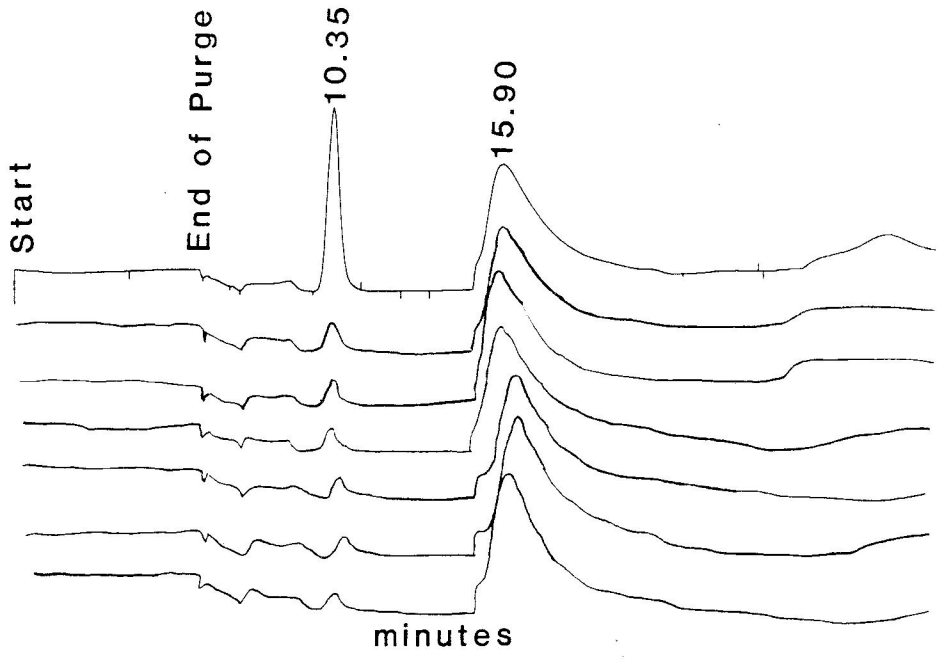

FIGURE 7
Gas chromatograms from repetitive purge/trap analyses (top to bottom in sequence) of a 45-mg/L solution of 2,4-pentanedione in water.

References

1. T. A. Bellar and J. J. Lichtenberg, "Determining Volatile Organics at Microgram-per-Litre Levels by Gas Chromatography," *Journal of the American Water Works Association* **66**, 739-744 (1974).
2. *Federal Register*, Vol. 44, No. 233 (December 3, 1979).

LA-10642-PR
Progress Report

UC-41
Issued: May 1986

Occupational Health and Environment Research 1984: Health, Safety, and Environment Division

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