SYMPOSIUM ON DIRECT VAPOR ANALYSIS

Introduction

The capacity audience and active discussion of papers presented at the symposium attest to the widespread interest in direct analysis of food vapors. The ease with which vapor analyses may be performed motivates much of this interest. Determination of volatile flavor components by direct gas chromatographic analysis is an attractive alternative to classical methods employing distillation, extraction, adsorption, or other techniques for sample preparation. Sample handling is minimized, thereby reducing the probability of artifact formation. Time required for sample preparation is reduced manyfold, affording the capacity to handle more samples and to examine effects of important experimental variables on vapor composition in applied technological investigations. Elimination of sample preparation procedures eliminates the variability associated with multi-step methods and renders direct vapor analysis very attractive as a quantitative approach in flavor studies. Moreover, the vapor phase above a food must contain the olfactory stimuli responsible for the subjectively perceived odor. Composition of this mixture of stimuli can be related to sensory response if those components which influence odor are detectable and measurable.

The limitations of available instruments fix the minimum quantity which can be detected by direct vapor analysis. Increasing sample size will reduce the minimum detectable concentrations of those moderately volatile components that influence flavor. The ability to increase the volume of vapor samples while retaining chromatographic resolution represents a major advance in direct vapor analysis. The symposium speakers presented a number of approaches and solutions to this problem. Vapor analysis has been employed for identification of components by combined gas chromatography-mass spectrometry. Methods for handling these large vapor volumes and for minimizing interference from water vapor provided topics of lively discussion.

All aspects of vapor analysis ranging from fundamental studies of solution–vapor partition to applications in food quality assessment were discussed. The papers presented represent the current state of the art. On behalf of the Flavor Subdivision, I wish to thank the speakers whose outstanding presentations contributed to the success of the symposium. The papers presented here will be of great value to the advancement of flavor research.

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Some Considerations of the Volatilities of Organic Flavor Compounds in Foods

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As water is the major constituent of most foods, some idea of the relative volatilities of flavoring compounds in foods can be obtained by consideration of their volatilities in water. For many compounds, volatilities can be calculated from published activity coefficients or solubilities and vapor pressures. In many other cases, however, this information is not available and there is need for experimental determination of volatilities in water solution. Experimental values obtained by the authors for homologous series of aldehydes, ketones, and esters agree fairly well with calculated values. Both calculated and experimental data show that for those series studied the relative volatility in very dilute solution increases as the carbon chain gets longer. However, the maximum concentration that can be obtained for any compound in the vapor is limited by the vapor pressure of the pure compound at that temperature.

When we place a food in a closed container, we might expect the volatile flavor compounds of the food to reach an equilibrium between the food itself and the atmosphere above the food. The factors controlling this equilibrium in foods which contain reasonable amounts of both fat and water, such as a fatty steak, could be very complex. But many foods, and particularly beverages, can be considered to be fairly homogeneous and consist of 50–90% water.

Because of this high percentage of water, it is conceivable that we can get some understanding of how organic flavor compounds behave in these foods by considering their volatilities in water.

A thorough treatment of volatilities of organic compounds in water solution could be quite complex, but if we consider solutions at constant temperature (25° C) and pressure (760 mm) and consider that we are generally dealing with relatively dilute solutions (less than about 1%), then the relations are fairly simple.

The main factor controlling the vapor solution equilibrium in a dilute water solution of a single organic compound is essentially a form of Henry's law. Henry's law, of course, states that the partial pressure of a particular component in the vapor above a solution is directly proportional to the component's concentration in that solution (cf., Lewis and Randall, 1961). This can be expressed as

$$p = C \times N \tag{1}$$

Alcohol	p/N	Air/water partition coefficient
Methyl	184	1.8×10^{-4}
Ethyl	218	2.1×10^{-4}
Propyl	291	2.8×10^{-4}
Butyl	360	3.5×10^{-4}
Pentyl	547	5.3×10^{-4}
Hexyl	649	6.3×10^{-4}
Heptyl	798	7.7×10^{-4}
Octyl	1020	9.9×10^{-4}

where p is the solute's partial pressure above the solution, C is a constant, and N is the molar fraction of the solute in the solution (*i.e.*, number of moles of solute over the total number of moles of water and solute). This relation in one form or another is fairly commonly used by workers using direct vapor analyses. One of the first to apply it to foods was Weurman (1961).

A convenient factor which follows from Henry's law is the air/water partition coefficient. This is simply the ratio of the concentration of the solute in the vapor over its concentration in the solution at equilibrium.

air/water partition coefficient $= K =$

$$\frac{\dfrac{\text{weight of solute}}{\text{per ml of air}}}{\dfrac{\text{weight of solute}}{\text{per ml of solution}}} \text{ at } 25° \text{ C} \quad (2)$$

For the present work we will only consider solutions at 25° C. We can also write eq 2 in the terms used for Henry's law.

$$K = \frac{p}{N} \times 0.97 \times 10^{-6} \quad (3)$$

The partial pressure p replaces the concentration in the vapor and the mole fraction N replaces the concentration in the solution. The value 0.97×10^{-6} combines the factors which are needed to convert concentration terms to pressure and mole fraction terms using gas laws, etc. The molecular weight of the solvent water is combined in this value but the molecular weight of the solute cancels out. From simple algebraic rearrangement of eq 1, it can be seen that p/N is equivalent to the Henry's law constant C.

In a study with hexanal and heptan-2-one (Buttery *et al.*, 1969), we found Henry's law quite valid over the range of from a few parts per million up to the point of saturation of these compounds in water, which was 0.5% for hexanal and 0.4% for heptan-2-one. Other workers (Weurman, 1961; Özeris and Bassette, 1963) have also demonstrated the validity of Henry's law for similar solutions.

Early Studies. Some of the first studies on the volatilities of organic compounds in dilute water solution were carried out by Butler and coworkers in 1935. They studied the homologous series of normal aliphatic alcohols from methanol to octanol. Their results are listed in Table I. Surprisingly, they found that the higher members of the series, such as octanol, were more volatile in dilute water solution than the lower homologs, such as methanol. Much of Butler's results was, however, obtained by calculation from other data rather than by direct experiment. We can express Henry's law as

$$p = p^0 \times \gamma \times N \quad (4)$$

where p^0 is the vapor pressure of the pure solute at 25° C and γ is the activity coefficient of the solute in water (*cf.*, Lewis and Randall, 1961). One can see by rearranging the equation that $p^0 \times \gamma$ is equal to p/N and replaces the Henry's law constant C in eq 1. For slightly soluble compounds we can replace γ by $1/N_s$, where N_s is the solubility of the compound in water expressed in mole fraction terms. This is the relation which Butler *et al.* (1935) used to determine the volatilities of the C_6–C_8 alcohols shown in Table I.

$$p = p^0 \times \frac{1}{N_s} \times N \quad (5)$$

We might note that Raoult's law is a special case where γ and N_s are equal to 1, when the solute is completely miscible with the solvent.

Probably the most useful work on the volatilities of organic compounds in water solution was published by Pierotti *et al.* (1959). Actually they were not particularly interested in the volatilities of organic compounds in water solution. Their main interest was in the determination of the activity coefficients of a wide variety of organic compounds in water and other solvents. One can see from eq 4 that if we know the vapor pressure of the pure material p^0, and its activity coefficient γ, we can then obtain the Henry's law constant C which is the same as p/N. As is shown in eq 3, this can be readily converted to the air/water partition coefficient. Pierotti *et al.* (almost as an afterthought in their 1959 paper) used such calculation of the product of γ and p^0 to plot volatilities against carbon number for homologous series of paraffins, ethers, ketones, alcohols, and acids in dilute water solution. Their calculations showed an increase in volatility with increasing carbon number, for several homologous series, similar to that which Burton and coworkers had obtained for the homologous alcohols.

Since many of the data of Pierotti and Burton concerning the volatilities of organic compounds in dilute water solutions were obtained essentially indirectly by calculation, it seemed desirable to verify this by experimentation on actual vapor-water solution systems. The availability of the gas chromatography flame ionization detector in early 1960 provided a relatively simple experimental method for doing this. Some early experimental work related to foods in this area was carried out by Nawar and Fagerson (1962), Burnett and Swoboda (1962), Jennings (1965), Reymond *et al.* (1966), Weurman (1961), Kepner *et al.* (1964), and other workers. Some more recent work has also been published by Nelson
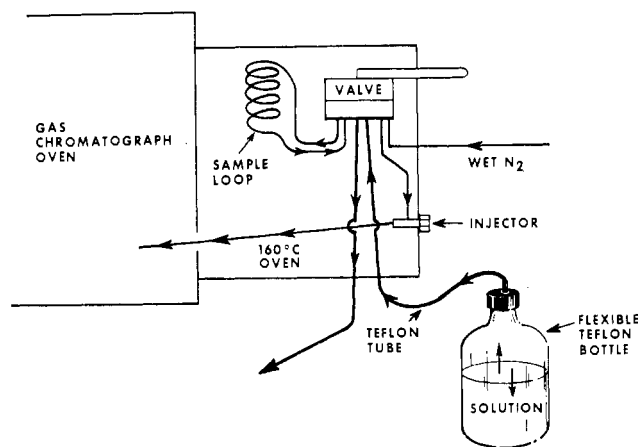

Figure 1. Apparatus used for introducing vapor and solution samples into the gas chromatograph
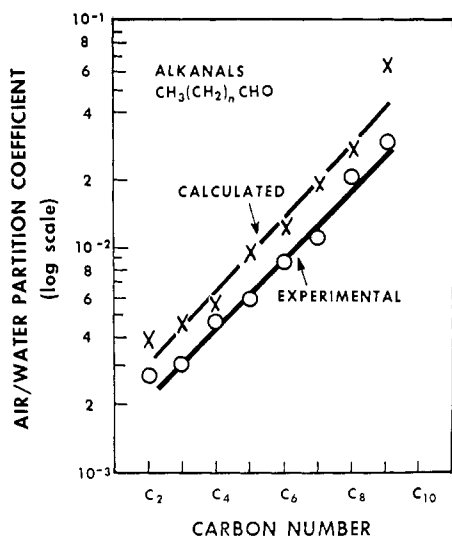
Figure 2. Comparison of calculated and experimental air/water partition coefficients for normal alkanals (at 25 ° C)

Figure 3. Comparison of calculated and experimental air/water partition coefficients for 2-alkanones (at 25 ° C)

and Hoff (1968). A method that we (Buttery *et al.*, 1969) applied to determine air to water partition coefficients is illustrated in Figure 1. A somewhat similar heated gas valve system had been used earlier by Burnett (1963). The solution is placed in a Teflon bottle and allowed to reach equilibrium in a 25° C constant temperature bath with occasional swirling of the bottle. Experiments showed that a 30-min period was quite adequate for equilibrium to be brought about. The vapor is then forced into the heated gas sampling loop by squeezing the bottle. The valve is then activated and a known volume of vapor introduced into the gas chromatograph. The use of Teflon and the heated sampling system is important in reducing adsorption effects, which can be quite large for the higher molecular weight compounds. A known volume of solution is injected alternately with the injection of vapor. The air/water partition coefficient can then be calculated from the areas of the vapor and solution peaks and the volumes injected. Results that we obtained using this method with some homologous series of esters, aldehydes, and ketones were reported previously (Buttery *et al.*, 1969).

These experimental results confirmed the predictions of Pierotti and Butler and coworkers that with each homologous series there is an increase in the air/water partition coefficient and hence volatility as the carbon chain gets longer. The methyl esters and aliphatic aldehydes are the most volatile series, with methyl ketones rather intermediate, and alcohols the least volatile. We were unable to get any reliable experimental results for free organic acids. Calculations from the data of Pierotti *et al.* (1959) showed that they would be about ten times less volatile than the corresponding alcohol homologs.

Calculation of Volatilities. The experimental results (Buttery *et al.*, 1969) compare fairly well with those calculated from the data of Pierotti *et al.* (1959) by Bomben and Merson (1969) who have made a thorough theoretical treatment of the volatilities of organic compounds in water solution.

Figure 2 compares the experimental values that we found for aliphatic aldehydes with those calculated by Bomben and Merson. There is a definite consistent difference, but it is almost within experimental error. Figure 3 shows a similar comparison for experimental and calculated values for methyl ketones. Again the difference is generally small; however, there is a fairly large deviation in the calculated value for the
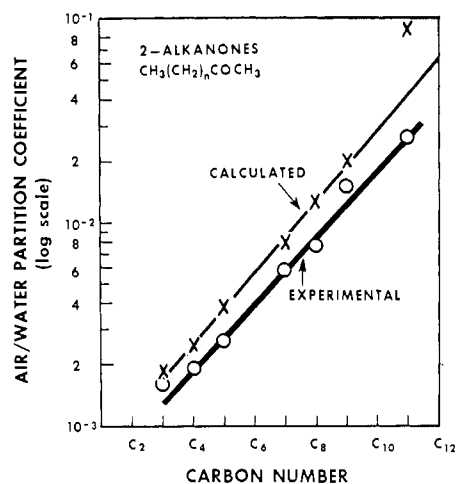
C_{11} compound undecan-2-one. This is probably due to the fact that it is difficult to obtain accurate figures on its very low vapor pressure.

To calculate the values that we have used in Figures 2 and 3, Bomben and Merson obtained vapor pressures of pure compounds from literature values (Jordan, 1954) and the use of Cox charts (Dreisbach, 1952). They obtained the activity coefficients from the following formula of Pierotti *et al.*

$$\log (\text{activity coefficient}) = A + B \times n + C/n \qquad (6)$$

where n is the number of carbon atoms in the molecule, and A, B, and C are constants for the particular homologous series. Pierotti *et al.* listed these constants for 18 different types of homologous series, including alkanals, alkan-2-ones, aliphatic esters, and acids, and also for some less common series such as alkyl cyanides.

Thus, for many compounds, we can calculate reasonably accurate air/water partition coefficients from information already available in the literature. For many other groups of compounds, however, the only way to get this information is by experiment. Table II lists some values obtained for some unsaturated aldehydes and some alkyl pyrazines. As might be expected, the introduction of conjugated double bonds increases the water solubility of the aldehydes and therefore lowers their volatility in water solution. The alkyl pyrazines are quite soluble in water. Because of this, their volatilities in water are relatively low, slightly less than that

Table II. Air/Water Partition Coefficients Found for Some Unsaturated Aliphatic Aldehydes and Alkyl Pyrazines at 25° C

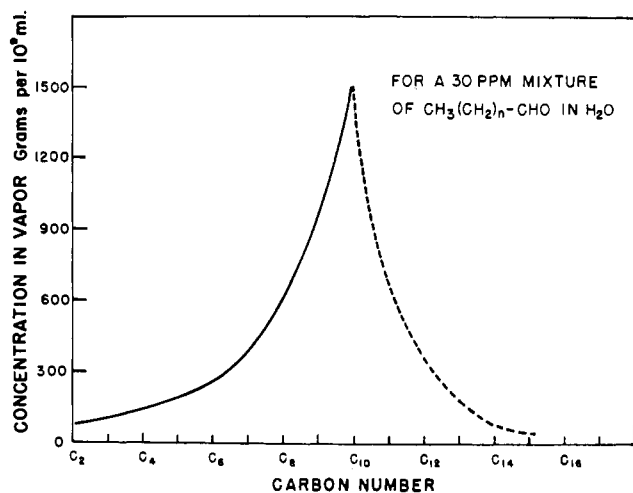| Compound	Air/water partition coefficient (25 ° C)
But-*trans*-2-enal	8×10^{-4}
Hex-*trans*-2-enal	2×10^{-3}
Oct-*trans*-2-enal	3×10^{-3}
Hexa-*trans,trans*-2,4-dienal	4×10^{-4}
2-Methylpyrazine	9×10^{-5}
2-Ethylpyrazine	10×10^{-5}
2-Isobutylpyrazine	2×10^{-4}
2-Ethyl-3-methoxypyrazine	6×10^{-4}
2-Isobutyl-3-methoxypyrazine	2×10^{-3}

Figure 4. Theoretical plot of the equilibrium concentration in the atmosphere above water containing 30 parts per million of each normal aliphatic aldehyde (at 25° C)

of the aliphatic alcohols. Again, however, increasing the alkyl side chain increases the volatility in water solution. Rather surprisingly, the introduction of a methoxy group increases the volatility about five to ten times. This may have something to do with the donation of electrons to the ring by the methoxy group.

Limiting Concentration in the Vapor. From such relations, as shown in Figures 2 and 3, we might expect that a plot of the concentration of a homologous series in the vapor, for a fixed concentration in the solution, would increase indefinitely as we increase the carbon number. For example, we might expect a C_{18} aliphatic aldehyde to be considerably more concentrated in the vapor than acetaldehyde when they are both at the same concentration in the water solution. However, this would only be true if we considered infinitely dilute solutions. Practical concentrations of flavor compounds in foods are not infinitely dilute and are roughly of the same order as the solubility of the C_{10} to C_{15} aldehydes.

It is interesting to see what happens in theory, if we take a homologous series such as the normal aliphatic aldehydes and consider each in water at a fixed concentration. If we chose 30 parts per million as this fixed concentration (the solubility of decanal in water), then a plot of the concentration in the vapor against carbon number at 25° C would give us a curve such as is shown in Figure 4. The concentration in the vapor

of aldehydes with carbon chains shorter than decanal would drop off according to their air/water partition coefficients. However, the higher aldehydes, being less soluble than decanal, would exist in the water in their free states. Their concentration in the vapor would drop off rapidly according to p^0 (the vapor pressure of the pure materials). There is of course nothing unusual about decanal. Such a curve would reach a maximum for any aldehyde whose solubility we took as the fixed concentration. For a 1 part per billion (10^9) solution, this maximum would correspond to about C_{16}. As we moved to the higher aldehydes the height of the maxima would get smaller and smaller and would always correspond to the vapor pressure of the pure aldehyde. The partial pressure p of the solute above the solution can, of course, never be greater than the vapor pressure p^0 of the compound in the pure state. This can readily be seen from eq 5. Thus, despite their higher air/water partition coefficients the higher homologs are always limited in how concentrated they can be in the vapor.

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