Title

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Journal

Chemical Senses, 28

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Publication Date

2003

Chemical Senses **28**:467-477, 2003

Quantification of Chemical Vapors in Chemosensory Research

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Abstract

Studies of olfaction and chemesthesis often rely on nominal, liquid-phase dilutions to quantify the chemicals tested, even though the associated vapor concentrations constitute the actual stimuli. For more than a decade now, our systematic studies of the olfactory and chemesthetic potency of members of homologous chemical series have routinely included quantification of vapors via gas chromatography. This article depicts the relationships between liquid- and vapor-phase concentrations for 60 volatile organic compounds (VOCs) and summarizes the theoretical and technical factors influencing these relationships. The data presented will allow other investigators working with these materials to express them as vapor concentrations even when lacking the resources to perform the analytical measurements. The paper represents a step toward creation of a practical archive for vapor quantification in chemosensory science.

Key words: Vapor/Liquid Concentration Relationships — Olfactometry — Gas Chromatography - Odorous Vapor Quantification - Irritant Vapor Quantification

Introduction

The scientific study of olfaction and chemesthesis (i.e., chemical sensory irritation) inevitably requires some attempt to deliver controlled amounts of chemical vapors. Control of concentration may occur via static or dynamic means (Cain et al., 1992). In static olfactometry the stimulus vapor is presented from the headspace of an enclosed container (e.g., a squeeze bottle or a glass vessel) whereas in dynamic olfactometry the stimulus vapor flows continuously in a carrier gas (e.g., nitrogen or odorless air). In the case of static control, an investigator may make the assumption that the number of molecules present in the vapor phase at steady state follows Raoult's law for ideal solutions or Henry's law for ideal dilute solutions. These laws assume proportionality of concentration in the headspace above a solution to mol fraction of solute. A solution ten times less concentrated than another should have tenfold fewer molecules in the headspace.

From time to time, a chemist may remind chemosensory investigators that it is not uncommon to observe deviations from these laws of proportionality (Haring, 1974). Depending upon interactions between solute and solvent, the concentration of a volatile organic compound (VOC) may sometimes exceed expectations, so-called positive deviations, and may sometimes lie below them, negative deviations. Without knowledge of whether one or another such deviation has occurred, an investigator may need to limit the conclusions of a study or may even promulgate an incorrect answer.

It remains rather common for investigators to express the magnitude of the chemosensory stimulus in nominal or relative terms. Nominal expression normally takes the form of specification of a liquid dilution, such as, a 0.1 %v/v solution of 1-butanol in mineral oil. An investigator who reads about this nominal stimulus may wish to use another solvent, such as water, and may wonder if the same nominal concentration will lead to the same number of molecules in the headspace (Tsukatani et al., 2003). One can readily invent scenarios where investigations will lead to incompatible results because of such matters. Undoubtedly, investigators have sometimes failed to take opportunities for direct comparison of their work with that of others when they feel insecure about whether their vapor-phase concentrations match that of others.

Measurement of the headspace above solutions for a wide range VOCs became feasible in the 1960's with availability of commercial gas chromatographs (GCs). Five decades have led to many improvements in this and other technologies for analysis of vapors, but three matters plague its application in chemosensory research: 1) expense, for a GC system will often cost upwards of $20,000, 2) the need for a sophisticated operator, and 3) the labor-intensive nature of the work. Specification of headspace concentration for a series of dilutions may entail days of work for a knowledgeable operator. Even then, the sensitivity of the instrument may not extend to the low concentrations used in an olfactory experiment. Faced with the expense, lack of expertise, consumption of time, and eventual need to extrapolate anyway, an investigator may opt not to measure concentration and merely to express it nominally. Is the decision defensible? Perhaps. Does it hold back advances in chemosensory science? Inevitably.

During the year 2002, some chemosensory investigators outside the field of human psychophysics realized that studies from the Chemosensory Perception Laboratory have typically entailed actual measurement of concentration and, further, that calibration curves for headspace concentrations might exist for various VOCs of interest, such as aliphatic alcohols, ketones, esters, and so on. The potential usefulness of the data to these investigators has led to the present attempt to make the information and the experiences of more than a decade of measurement available more generally. The core of the results presented below describes the relationship between liquid- and vapor-phase concentrations for three dozen chemicals from six homologous chemical series — as has been found using techniques of static olfactometry — and discusses the trends and factors that influence these relationships. The data for these chemicals could serve as the nucleus of an archival set to enable investigators to calculate vapor-phase concentration for solutions of VOCs. Whereas the present report focuses upon issues largely pertinent to static olfactometry, another focuses upon issues pertinent to dynamic olfactometry (Schmidt and Cain, 2003).

Materials and Methods

Stimuli. All chemicals were analytical grade reagents. They included homologous n-alcohols: propanol, butanol, hexanol, and octanol; homologous acetates: methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, decyl and dodecyl acetate; homologous 2-ketones: propanone (i.e., acetone), pentanone, heptanone, and nonanone; homologous alkylbenzenes: methyl (i.e., toluene), ethyl, propyl, butyl, pentyl, hexyl, heptyl, and octyl benzene; homologous aliphatic aldehydes: butanal, pentanal, hexanal, heptanal, and octanal; and homologous carboxylic acids: methanoic (i.e., formic), ethanoic (i.e., acetic), butanoic (i.e., butyric), hexanoic, and octanoic acid. The solvent was mineral oil (light, Food Chemicals Codex quality) except for 1-propanol, 2-propanone, formic acid, and acetic acid, where it was distilled water. 1-Butanol was tested in both solvents.

Equipment. Vapor-phase concentrations were measured in Hewlett-Packard 5890 gas chromatographs (GCs) with a flame ionization detector (FID) or a photoionization detector (PID). The GCs were equipped with a gas-sampling valve (0.25 or 1.00 ml sampling loop). Pre-concentration of chemicals (e.g., Cometto-Muñiz et al., 2003) was accomplished by using a gas-tight syringe to load samples of vapor into an adsorption tube and, later, thermally desorbing it in a Thermal Desorption Unit (ACEM Model 900, CDS Analytical, Inc.) whose output fed a GC. We employed Sorbent Tubes, 4.5 in L x 4 mm ID, packed with 20-35 Tenax-TA/Carboxen1000/CarbosieveSIII. The GC signal was integrated by a Hewlett-Packard 3390A or 3396A integrator, or by an STD MacLab A/D Converter (MacLab version 3.5, Chart version 3.5.6, Scope version 3.5.6, and Peaks version 1.4). The GC columns used were a DB-1, 30 m x 0.53 mm ID, used alone or in series with a DB-WAX, 30 m x 0.53 mm ID (both from J&W Scientific), and, for the carboxylic acids, an HP-FFAP, 30 m x 0.53 mm ID, 1.0 µm film thickness (from Hewlett-Packard). The coefficient of variation of replicate gas chromatographic measurements across VOCs and concentrations typically averaged around 10% (e.g., Cometto-Muñiz et al., 2000) and ranged from 5% (e.g., Cometto-Muñiz et al., 2002) to 13% (e.g., Cometto-Muñiz et al., 2003).

Vapors were sampled from the headspace of either 270-ml plastic squeeze bottles (see Cain, 1989; Cometto-Muñiz and Cain, 1990) or 1,900-ml glass vessels adapted for nasal (Cometto-Muñiz et al., 2000) or ocular (Cometto-Muñiz et al., 2001) chemosensory stimulation. To minimize the potential for depletion of the headspace concentration of the containers we have prepared a number of replicas for each concentrattion (from two to five replicas used sequentially) and have shaken the containers in a circular fashion to speed up re-equilibration (Dravnieks, 1975). Nevertheless, a comprehensive and strict quantitative appraisal of this potential problem awaits further research.

Results and Discussion

1) Relationship between liquid and vapor concentrations

Throughout systematic studies of odor, nasal pungency, and eye irritation thresholds along and across homologous chemical series (see reviews in Cometto-Muñiz, 2001; Cometto-Muñiz and Cain, 1996), we have gathered a considerable amount of data on the relationship between liquid-phase concentration (in %v/v) and vapor-phase concentration (in ppm by volume). Across the entire concentration range, the vapor pressure (P_{st}) of a solute in solution with a solvent is given by Raoult's law for an ideal solution:

$$P_{st} = P^{\circ}_{st} * X_{st} \tag{1}$$

where P°_{st} is saturated vapor pressure of neat solute and X_{st} is mol fraction of solute. Often, solutions are not ideal and actual vapor pressure deviates from that calculated by Raoult's law. For dilute solutions, such as those used in olfactory and even chemesthetic research, Henry's law is relevant. This can be expressed in a number of ways, depending on the units used to describe the vapor and solution quantities of the solute. A common way to express Henry's law is:

$$P_{st} = H^{x} * X_{st} \tag{2}$$

However, it is also quite correct to define solute quantities as molar concentration in both the gaseous phase and the solution phase, leading to equation (3).

$$[C_{st}]_{vap} = H^{c} * [C_{st}]_{liq} \tag{3}$$

In both equation (2) and equation (3), H is Henry's constant for a particular solute, solvent, and temperature. It is worth noting that H^{c}, defined in equation (3), is the inverse of L, the Ostwald solubility coefficient.

In the figures presented below and in Table 1, we depict the following relationship:

$$[C_{st}]_{vap} = a\ [C_{st}]_{liq}^{ß} \tag{4}$$

where "a" is a constant. We express the concentration of the solute in liquid solution as %v/v, that is: $100^*[v_{st}/(v_{sv} + v_{st})]$, where v_{st} is the volume of the solute and v_{sv} is the volume of the solvent. If v_{st} is small compared to v_{sv}, the expression reduces to: $100^*(v_{st}/v_{sv})$ where v_{sv} is effectively a constant. Then equation (4) will take the form:

$$[C_{st}]_{vap} = a_1\ (100^*v_{st})^{ß} \tag{5}$$

with "a_1" as a new constant. Collecting up constant terms into a new constant "a_2" and noting that vapor concentration can be expressed as pressure, we have:

$$P_{st} = a_2\ (v_{st})^{ß} \tag{6}$$

Now, v_{st} simply reflects the concentration of the solute in liquid solution, so:

$$P_{st} = a_3\ [C_{st}]^{ß} \tag{7}$$

If the exponent ß is unity, as it typically is, we have:

$$P_{st} = a_3\ [C_{st}] \tag{8}$$

which is simply another way of expressing Henry's law, equations (2) and (3). Thus, equation (4) for dilute solutions is the standard Henry's law when ß = 1.

In early work, we relied on the assumption that published values of vapor pressure provided an accurate estimate of saturated vapor concentration above neat

VOC. We expressed vapor concentrations of our dilution series based on GC readings relative to these estimates. As discussed below, we eventually saw risks from relying on a single bibliographic source for a value of vapor saturation and began exploring a number of sources for each substance in order to select the most reliable data, particularly data corresponding to experimental measures of the saturated vapor as opposed to data calculated from fitted equations.

Figure 1 shows, for four homologous n-alcohols, the relationship between the concentration in the liquid phase and concentration of vapor in the headspace above the source. The latter concentration is the actual stimulus presented to subjects. It is important to report the solvent used to prepare the dilution series since, as illustrated below, the same liquid dilution of a certain chemical will very likely produce different vapor concentrations above the solution depending on the solvent used. In the case of the alcohols depicted in Fig. 1, the solvent used for 1-propanol was distilled water, whereas the solvent used for the other homologs was mineral oil. In Figure 1 and Table 1, all alcohols showed slopes near unity, i.e., showed simple proportionality between liquid and vapor concentration. Another characteristic of these functions is a departure from simple proportionality for relatively high liquid concentrations, commonly above 1 to 10 %v/v. Departures from proportionality might also appear at very low liquid concentrations and they can be attributed to having reached the limit of sensitivity of the GC. Accurate measurements of vapor concentrations at and below these low levels would require accumulation of the mass of the stimulus, for example, on an adsorbent material and later desorption into the GC. We will address this technique below.

Insert Figure 1 and Table 1 about here

Figure 2, panels “a” through “g” present similar graphs to Figure 1 for homologous acetate esters, 2-ketones, alkylbenzenes, aliphatic aldehydes, and carboxylic acids. Similar considerations regarding proportionality between liquid- and vapor-phase concentrations apply here. Deviations at the higher end of the range were often observed. Again, an exponent close to unity characterized all functions (see also Table 1). Nevertheless, the largest homologs in some of the series — for example, octyl and higher acetates, and octyl benzene — tended to show a flattening of their slope. Henry's law only applies across the entire liquid concentration range if the two components form an ideal mixture according to Raoult's law. Usually, positive deviations from Raoult's law are observed; in that case, the observed Henry's law constant would become smaller as the solute liquid concentration becomes larger, exactly as we observe.

Insert Figure 2 about here

Direct injection of an aliquot of the headspace from the stimulus-container into the GC was done with either a gas-sampling valve or a gas-tight syringe. The heavier stimuli (i.e., long carbon chain members) may tend to adsorb to the sampling loop of the gas sampling valve. The measurements presented in Figures 1 and 2 were done using a gas-sampling valve. In more recent work, we have used gas tight syringes. Below we will discuss advantages and disadvantages of both methods and will show that, generally, they yielded comparable results.

Deviations from proportionality in the form of a downward concavity at the very high end of the functions (i.e., positive deviations from Raoult's law) were quite pronounced for the lower homologs in each series and tended to be less pronounced for the higher homologs. Table 1 shows the maximum concentration of each VOC that, in our conditions, still followed the proportional trend before the concavity appeared.

2) <u>Influence of the solvent</u>

With the few exceptions noted, the bulk of the data presented so far rests on solutions of the chemical of interest in mineral oil. As mentioned, it is necessary to take the solvent into account when deriving the vapor-phase concentration in equilibrium with a liquid-phase concentration (Tsukatani et al., 2003).

To illustrate the point, Figure 3 presents the vapor concentrations in equilibrium with a series of liquid dilutions of 1-butanol in either mineral oil or distilled water. Both dilution series were prepared in squeeze bottles. The series in water corresponded to the dilutions of 1-butanol used in the Connecticut Chemosensory Clinical Research Center (CCCRC) test of olfactory functioning (Cain, 1989; Cain et al., 1988). It is clear that, across the range of liquid concentrations explored, use of mineral oil produced higher vapor-phase concentrations than use of water. Nevertheless, note that the functions are approximately parallel, with exponents close to unity. Although the set of butanol in water does not include liquid concentrations above 4 %v/v, the trend of the relationship will necessarily have to curve at higher values because the vapor-phase concentration of 1-butanol cannot exceed the saturated vapor concentration, approximately, 8,057 ppm. In summary, we can expect that below a certain liquid concentration the relationship between liquid and vapor concentration of a solute in a solvent will be approximately proportional, but the actual value of the vapor-phase concentration will depend on interactions between the particular solute and solvent. For 1-butanol in water and 1-butanol in hexadecane (a surrogate for mineral oil), Henry's constant (H^c in equation (3)) is $3.5*10^{-4}$ and $25.0*10^{-4}$ respectively, i.e., a factor of 7.1, showing how a change of solvent can lead to quite different solute vapor pressures (Abraham et al., 1994). The intercept in the equation for 1-butanol in water and in mineral oil (Table 1) differ by a similar factor, 7.7.

Insert Figure 3 about here

3) Calibration of vapor-phase vs. liquid-phase concentration functions

a) Using the value of vapor saturation of the chemical.

GC readings, which typically quantify an area under a curve, do not express values of concentration per se. They need to be calibrated to indicate actual concentrations. One strategy is to tie a GC reading to a known vapor concentration and, then, use the resulting factor to convert all other GC readings. A good reference concentration can be the saturated vapor concentration of the chemical at room temperature and normal atmospheric pressure. Such a reference has two important advantages: First, the value can be obtained from handbooks or databases, and, second, it can be prepared easily. Its preparation simply involves placing neat chemical into a container.

We have found that not all sources will agree on the vapor pressure of a chemical at a given temperature. This was surprising since vapor pressure is a fundamental physicochemical property. An extreme example occurred for the vapor pressure of octanal. The value calculated at 23 °C from tabular information in the Handbook of Chemistry and Physics (Weast, 1981-1982) equaled 0.0053 mmHg, corresponding to a saturated vapor concentration of 6.97 ppm. The value obtained from other handbooks (Beilstein, 1984; Stephenson and Malanowski, 1987) equaled 2.14 mmHg, corresponding to a concentration of 2,816 ppm, 404 times higher. Values of vapor pressure from the Handbook of Chemistry and Physics come from fitted equations and may rely on very old experimental data, where the purity of the chemical is unknown. In some cases, the measurements may have been taken at temperatures far from ambient and errors of extrapolation may be sizable.

This example of a difference of more than two orders of magnitude might occur infrequently, but in other cases the difference has approached one order of magnitude, hardly a trivial amount. For hexanoic acid, for example, the Hazardous Substances Data Bank (HSDB)–TOXNET cites a vapor pressure of 0.20 mmHg at 20°C whereas (de Kruif et al., 1982) cite a value of 0.031 mmHg, about six times lower.

To illustrate the disparities, we compare in Table 2 the values of saturated vapor pressure at room temperature retrieved by the authors at the University of California, San Diego and the author at University College London.

Insert Table 2 about here

In summary, if one needs to rely on a reported value of saturated vapor concentration, the safest strategy is to find more than one source and choose the value that appears more reliable. Such a task can often be hard to accomplish. If one cannot arrive at a reliable value for vapor saturation at room temperature, it is necessary to create a calibration curve based on injection of known masses of chemical into the GC. It is hard to argue against such direct calibration in all cases, even though it entails extra work.

b) Building of a calibration curve for mass

Chromatographic analysis of liquid samples of known masses of VOC can obviate reliance on archived values of vapor pressure. The equation that describes the relationship of the GC reading to the mass in liquid samples can serve to transform GC readings of vapor samples into absolute concentration. Care should be taken to use the same chromatographic conditions of flow, temperatures, etc., in the creation of the calibration curve as in the analysis of the actual headspace samples. Instead of relying on an indirect calibration point, as does the previous method, this approach relies on direct and multiple calibration points selected to cover the range of GC readings expected from the dilution-step headspace samples. Figure 4 shows a calibration curve obtained for butyl acetate. The mass injected covers the range 3.8 to 3,752 ppm for vapor-phase samples of 0.250 ml.

Insert Figure 4 about here

4) Comparability of approaches and methods to establish vapor-phase concentration

Over time, we have switched from use of plastic squeeze bottles (e.g., Cometto-Muñiz et al., 1999) to use of glass vessels (e.g., Cometto-Muñiz et al., 2003; Cometto-Muñiz et al., 2001) that provide improved stimulus delivery and better chemosensory performance (Cometto-Muñiz et al., 2000). In terms of calibration strategy, we have always relied on gas chromatography (Cometto-Muñiz and Cain, 1990). Initially, we used the indirect calibration strategy based on the value of vapor saturation. More recently, when the focus of our studies progressed from testing groups of single compounds to testing binary mixtures, we switched to the direct calibration approach based on injection of known masses of chemical.

To sample headspace and introduce it into the GC, we started by using a gas-sampling valve, but now use mostly gas-tight syringes. A gas sampling valve allows volumes as large as 5 ml. A gas-tight syringe larger than 0.25 ml is often unpractical to use due to limitations of volume in the injection port and column of the GC. Against the advantage of a larger volume of sample, the gas sampling valve has the disadvantage of potential adsorption of the chemical on the stainless steel or nickel walls of the loop.

The sensitivity of the GC rarely poses an issue in studies of chemesthetic responses, where concentrations of vapors are high (see Cometto-Muñiz et al., 2001). It poses an issue more commonly in studies of olfactory responses, where concentrations are low. It becomes especially troublesome in the study of odor detection of mixtures where components might lie at even lower concentrations (see Cometto-Muñiz et al., 2003). In the case of mixtures, it is even more important to measure the vapor concentration of the components since it is not uncommon to observe deviations from theoretically predicted values (Haring, 1974). In such circumstances, we have employed pre-concentration of vapors followed by thermal desorption (Cometto-Muñiz et al., 2003). The method uses adsorbent-filled tubes that are loaded with quite large samples of headspace (e.g., 10 to 20 ml) by means of appropriate gas-tight syringes. The pre-concentrated samples are then thermally desorbed into the GC.

We have measured vapor/liquid concentration relationships in squeeze bottles, in glass vessels, via gas sampling valves, via gas-tight syringes, calibrated through the indirect single-point method, calibrated through the direct multiple-point method, for chemicals presented singly, and for chemicals presented in mixtures. Despite some variability underlying the use of different instruments and conditions, a relatively uniform vapor vs. liquid concentration relationship should emerge for any particular chemical, independently of the specific approach used to obtain it. Figure 5 panels “a” through “d” present such vapor vs. liquid concentration relationships, measured under the above mentioned variety of conditions, for the compounds 1-butanol, 2-heptanone, butyl acetate, and toluene, respectively. The results showed considerable uniformity. In the cases of butyl acetate (Figure 5c) and toluene (Figure 5d), readings from low concentrations in the range of odor detection were not possible through direct headspace sampling, so they were measured via pre-concentration and subsequent thermal desorption. Note how this outcome merged with that of the direct sampling techniques at higher concentrations.

Insert Figure 5 about here

As a rule, any compound should produce a consistent vapor vs. liquid concentration relationship irrespective of the particular procedure employed to calculate vapor concentrations and of the container from whence the sample is taken. To illustrate this, Figure 6 panels “a” through “c” show plots of vapor vs. liquid concentrations across members of homologous alcohols, acetate esters, and ketones, respectively. Despite the diversity of conditions, the relationship for each substance often held quite well. Nevertheless, there were instances where calibration based on a reported value of saturated vapor differed by more than a 25% amount from calibration using liquid injections. For example, this happened for 1-hexanol, hexyl acetate, octyl acetate, 2-pentanone, and 2-nonanone. If one cannot know whether the two approaches will agree, the investigator with the wherewithal to do chromatography should use the liquid injection for increased certainty. Thus, the value of the parameters reported in Table 1 for these five VOCs correspond to calibration by liquid injection.

Insert Figure 6 about here

Although we have developed the themes of this report around the members of six homologous series, we have assessed vapor-phase concentrations for other VOCs as well (Cometto-Muñiz and Cain, 1990; Cometto-Muñiz and Cain, 1993; Cometto-Muñiz and Cain, 1994; Cometto-Muñiz et al., 1998). The table in the Appendix shows the parameters for these in the same format as Table 1.

Summary and Conclusions

Based on GC measurements for three dozen VOCs from six homologous chemical series, we found that, as a general rule, there was a simple proportionality between the liquid- and the vapor-phase concentration of these VOCs when they were in equilibrium in a closed container. Nevertheless, deviations from proportionality were common for solutions above 1 to 10 %v/v. The most volatile members of a series (i.e., lower homologs) began to depart from proportionality at concentrations around 1 %v/v. As volatility decreased, departure from proportionality began only at higher concentrations, 10 %v/v or higher. Departures were also observed for the highest molecular weight compounds (e.g., decyl acetate, octyl benzene) and were likely due to deviations of the solutions from the behavior of an ideal mixture. Measurements obtained with 1-butanol exemplified how use of different solvents to dilute an odorant can alter the vapor concentration above a liquid solution although maintaining a proportional relationship. Specification of the concentration of vapors delivered as stimuli in studies on olfaction and chemesthesis can be accomplished by actual experimental measurement or by reliance on a dataset that has performed those measurements. Towards the aim of beginning to build such archival dataset, the present article presents the vapor-phase concentrations associated with a wide range of liquid dilutions for 60 VOCs commonly used as olfactory and chemesthetic stimuli.

Acknowledgments

Preparation of this article was supported by research grant number R01 DC02741 from the National Institute on Deafness and Other Communication Disorders, National Institutes of Health. Thanks are due to R. Loya, C. Sorensen, and C. Vo for excellent technical assistance.

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Figure Legends

Figure 1. Vapor (ppm by volume) vs. liquid (% v/v) concentration for homologous alcohols in logarithmic coordinates. Except where indicated, the solvent was mineral oil. The exponent ß (slope in the double logarithmic coordinates of the figure) is indicated for each VOC. See Table 1 for the specific values and applicable concentration range of the power equation for each chemical.

Figure 2. Analogous to Figure 1, but for homologous acetate esters (panels a and b), 2-ketones (panel c), alkylbenzenes (panels d and e), aliphatic aldehydes (panel f), and carboxylic acids (panel g).

Figure 3. Vapor (ppm by volume) vs. liquid (% v/v) concentration for 1-butanol with either mineral oil or distilled water as solvent. The slope (ß) of the fitted function is shown.

Figure 4. GC calibration curve for liquid-phase butyl acetate showing GC readings (V.sec) as a function of injected mass (μg). The equation of the curve is shown. Bars, sometimes hidden by the symbol, represent standard deviations.

Figure 5. Showing the agreement among vapor concentrations of a VOC, produced by the same liquid dilution, measured across different studies through the years, involving different conditions in terms of: odor-delivery containers, calibration strategies, GC sampling techniques, use or not of pre-concentration methods, and presence or absence of other chemicals in the sample (see text). Panels a, b, c, and d present the results for 1-butanol, 2-heptanone, butyl acetate, and toluene, respectively.

Figure 6. Showing the stability of relationships of vapor (ppm by volume) vs. liquid (% v/v) concentration for three homologous n-alcohols (panel a), acetate esters (panel b), and 2-ketones (panel c), under different conditions (see text). For all panels, conditions include: using squeeze bottles re saturated vapor concentration (squares), using glass vessels re saturated vapor concentration (circles), and building a calibration curve for mass (diamonds).

Table 1. Value of parameters from the relationship between liquid-phase ($[C]_{liq}$) and vapor-phase ($[C]_{vap}$) concentrations for the VOCs depicted in Figures 1 to 6. All relationships conform to a power function of the form: $[C]_{vap} = a.[C]_{liq}^{ß}$, and in the double logarithmic coordinates of the figures present a correlation coefficient of at least 0.99. Also shown is the maximum liquid concentration of each VOC that follows the relationship. The solvent was mineral oil, except where indicated within brackets.

VOC	Exponent (ß)	Constant (a)	Maximum concentration (%v/v)
1-Propanol (in H_2O)	1.02	499	10
1-Butanol (in H_2O)	1.04	5601	4
1-Butanol	0.95	727	0.4
1-Hexanol	0.94	429	1
1-Octanol	0.90	60	1
Methyl acetate	1.17	148568	1
Ethyl acetate	0.95	87434	1
Propyl acetate	1.02	18738	1
Butyl acetate	0.95	2461	1
Pentyl acetate	0.94	374	10
Hexyl acetate	0.91	48	10
Heptyl acetate	0.95	476	1
Octyl acetate	0.67	4.34	10
Decyl acetate	0.65	2.18	100
Dodecyl acetate	0.66	0.26	100
2-Propanone (in H_2O)	1.08	79655	1
2-Pentanone	1.19	5912	10
2-Heptanone	1.11	295	4

2-Nonanone	0.98	88	10
Toluene	1.00	1292	30
Ethyl benzene	0.99	686	10
Propyl benzene	1.03	65	10
Butyl benzene	1.03	42	10
Pentyl benzene	0.98	8.27	10
Hexyl benzene	1.02	2.13	10
Heptyl benzene	1.23	0.28	30
Octyl benzene	0.78	0.45	30
Butanal	1.13	210924	0.4
Pentanal	1.04	52789	1
Hexanal	1.05	1413	4
Heptanal	1.06	300	4
Octanal	1.02	140	10
Formic acid (in H_2O)	0.91	167	4
Acetic acid (in H_2O)	1.70	4.39	30
Butanoic acid	0.99	189	0.4
Hexanoic acid	0.95	6.51	1
Octanoic acid	1.20	0.024	100

Table 2. Values of saturated vapor pressure (P°) in the range 20 to 25 °C (exact temperature might differ among chemicals and sources) obtained independently, from different sources, by the authors at the University of California, San Diego (UCSD) and the author at University College London (UCL) for the 36 chemicals depicted in Figures 1 to 6. Also shown is the ratio from the 2 set of values. Differences between values for

the same chemical larger than about 25% might constitute excessive uncertainty for the outcome of some chemosensory studies.

Chemical	**P°(mmHg) UCSD**	**Source UCSD**	**P°(mmHg) UCL**	**Source UCL**	**P°(UCSD) / P°(UCL)**
Propan-1-ol	17	1	18	6	1.0
Butan-1-ol	6.1	1	5.4	6	1.1
Hexan-1-ol	0.97	1	0.55	6	1.8
Octan-1-ol	0.115	1	0.061	6	1.9
Methyl acetate	197	2	198	7,4	1.0
Ethyl acetate	87	2	86	6	1.0
n-Propyl acetate	29	2	30	6,4	1.0
n-Butyl acetate	9.9	2	10	6	1.0
n-Pentyl acetate	4.0	2	3.6	7	1.1
n-Hexyl acetate	1.5	2	1.2	4	1.2
n-Heptyl acetate	0.57	2	0.43	10	1.3
n-Octyl acetate	0.17	2	0.16	4	1.1
n-Decyl acetate	0.030	2	0.019	4	1.5
n-Dodecyl acetate	0.0042	2	0.0019	4	2.2
Propanone	200	1	212	6	0.9
Pentan-2-one	14	1	32	4	0.4
Heptan-2-one	1.3	1	3.3	4	0.4
Nonan-2-one	0.58	1	0.35	4	1.7
Toluene	26	2	26	8,9,7	1.0
Ethylbenzene	10	2	8.5	8,9,7	1.2
n-Propylbenzene	2.00	2	2.96	8,9	0.7
n-Butylbenzene	1.03	2	0.89	8,9	1.2
n-Pentylbenzene	0.28	2	0.28	8,9	1.0
n-Hexylbenzene	0.088	2	0.086	8,9	1.0
n-Heptylbenzene	0.028	2	0.025	8,9	1.1
n-Octylbenzene	0.0089	2	0.0069	8,9	1.3
butanal	92	3	101	6	0.9
pentanal	50	3	38	10	1.3
hexanal	11	3	13	10	0.8
heptanal	3.0	3	4.4	10	0.7
octanal	1.2	3	2.1	4	0.6
formic acid	35	3	39	4	0.9
acetic acid	11	3	14	7	0.8
butanoic acid	0.43	3	0.68	7	0.6
hexanoic acid	0.20	3	0.041	5	4.8
octanoic acid	0.0061	1	0.0040	5	1.5

1: (Weast, 1981-1982)

2: MSDS: Material Safety Data Sheets.

3: HSDB: Hazardous Substances Data Bank, TOXNET, National Library of Medicine.

4: (Stephenson and Malanowski, 1987)

5: (de Kruif et al., 1982)

6: (Boublík et al., 1984)

7: (Riddick and Bunger, 1970)

8: (Wilhoit and Zwolinski, 1971)

9: TRC Thermodynamic Tables, Thermodynamics Research Center, Texas A & M University Systems. College Station. Texas.

10: Interpolation from a plot of log vapor pressure vs. carbon chain length for that homologous series.

Appendix. Parameters of the relationship $[C]_{vap} = a.[C]_{liq}^{ß}$ (see Table 1) for additional VOCs in mineral oil (except when other solvent is indicated). Example: In a closed container, a 0.1 % v/v solution of 1,8 cineole in mineral oil ($[C]_{liq}$) would produce a headspace concentration ($[C]_{vap}$) having: 46. $(0.1)^{0.99}$ = 4.7 ppm of 1,8 cineole.

VOC	Exponent (ß)	Constant (a)	Maximum concentration (%v/v)
1,8 Cineole	0.99	46	30
Cumene	0.98	116	30
Linalool	0.91	55	4
p-Cymene	0.95	45	30
Geraniol	0.73	1.07	100
delta-3-carene	0.99	49	30
alpha-Pinene	0.89	92	100
beta-Pinene	0.91	79	30
alpha-Terpinene	0.90	34	100
gamma-Terpinene	0.88	41	10
S(-) Limonene	0.88	34	100
R(+) Limonene	0.94	39	30
2-Propanol (in H_2O)	0.87	1924	30
2-Butanol	0.85	10947	1
2-Methyl-2-propanol	0.96	41173	0.4
sec-Butyl acetate	1.03	4223	4
tert-Butyl acetate	0.98	11727	4
4-Heptanol	0.82	295	1
1-Octene	1.04	2557	4
1-Octyne	1.03	1424	4

Chlorobenzene	1.00	876	10
Pyridine	0.98	3495	10
Ethyl propanoate	1.02	2615	*
Ethyl heptanoate	0.81	28	40

* The relationship remained proportional up to the highest liquid concentration explored, 1 % v/v.

FIGURE 1

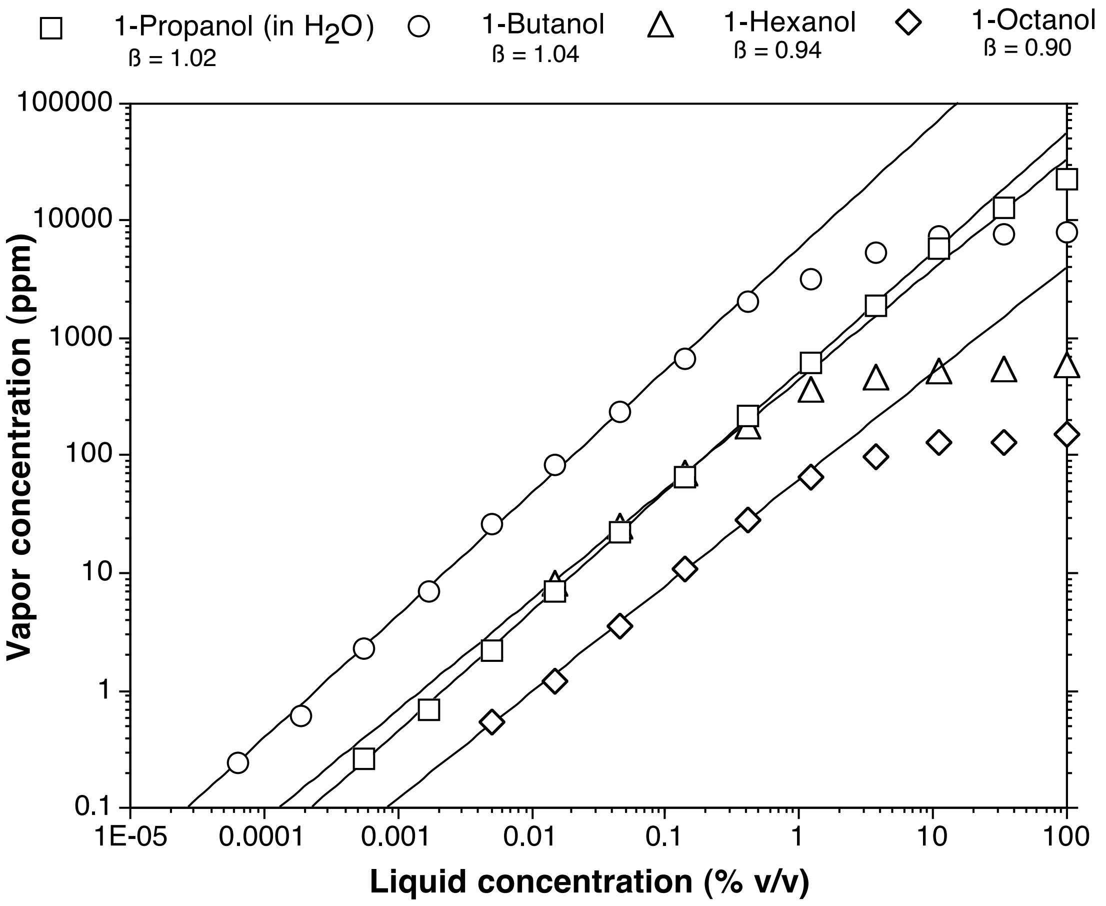

1-Propanol (in H_2O)
ß = 1.02
1-Butanol
ß = 1.04
1-Hexanol
ß = 0.94
1-Octanol
ß = 0.90
Vapor concentration (ppm)
100000
10000
1000
100
10
1
0.1
1E-05
0.0001
0.001
0.01
0.1
1
10
100
Liquid concentration (% v/v)

FIGURE 2 a)

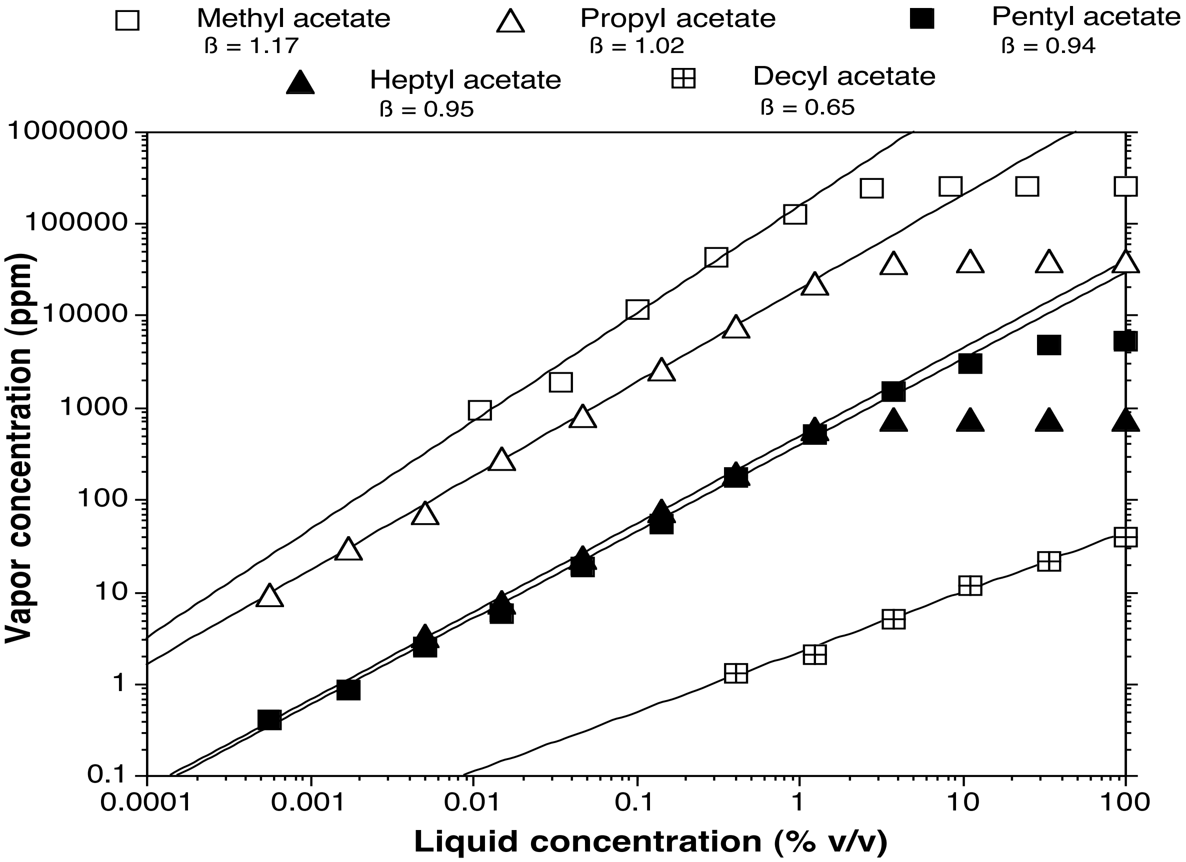


FIGURE 2 b)

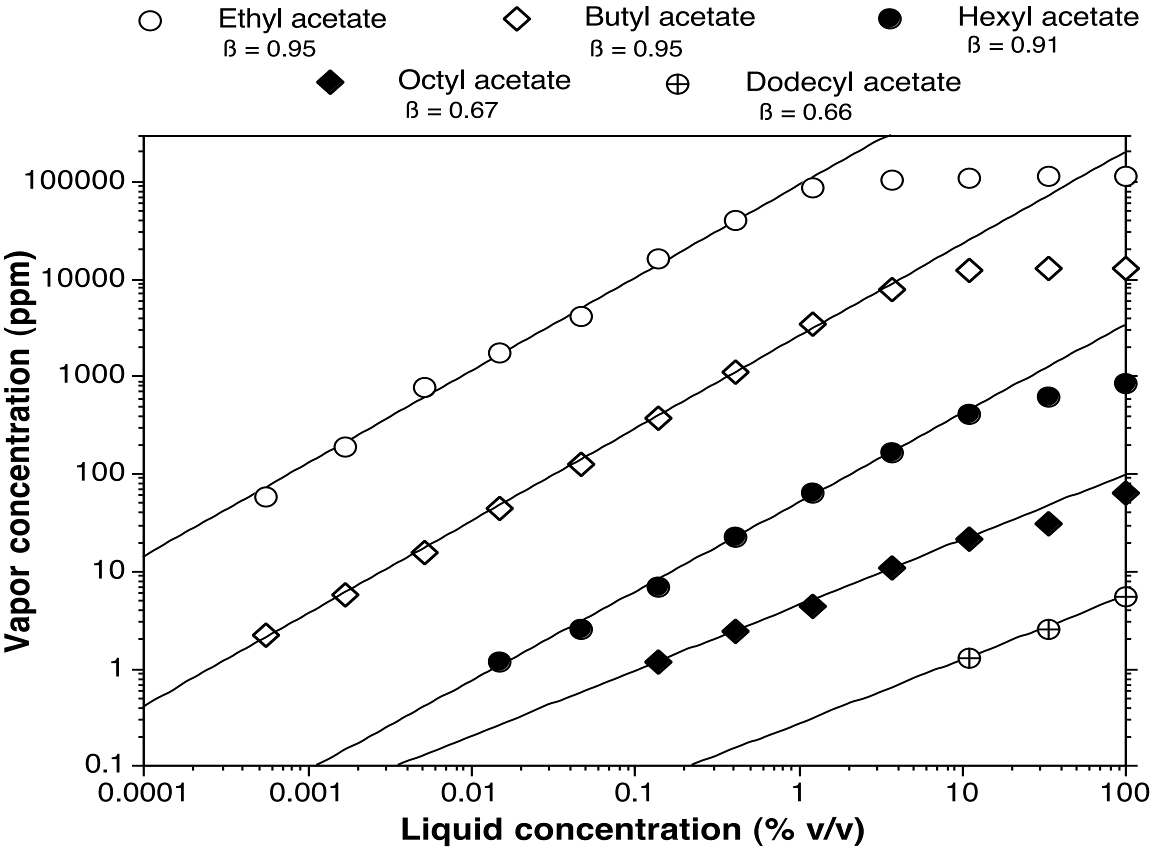


FIGURE 2 c)

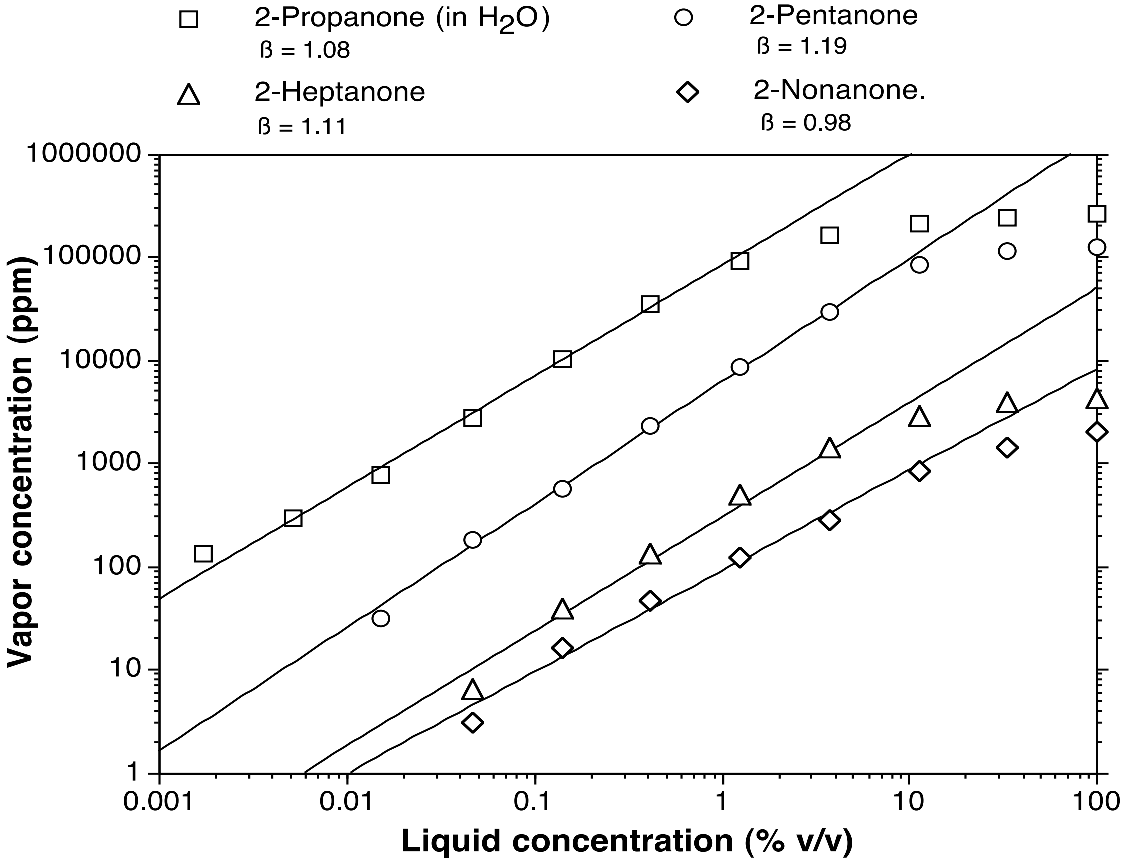


FIGURE 2 d)

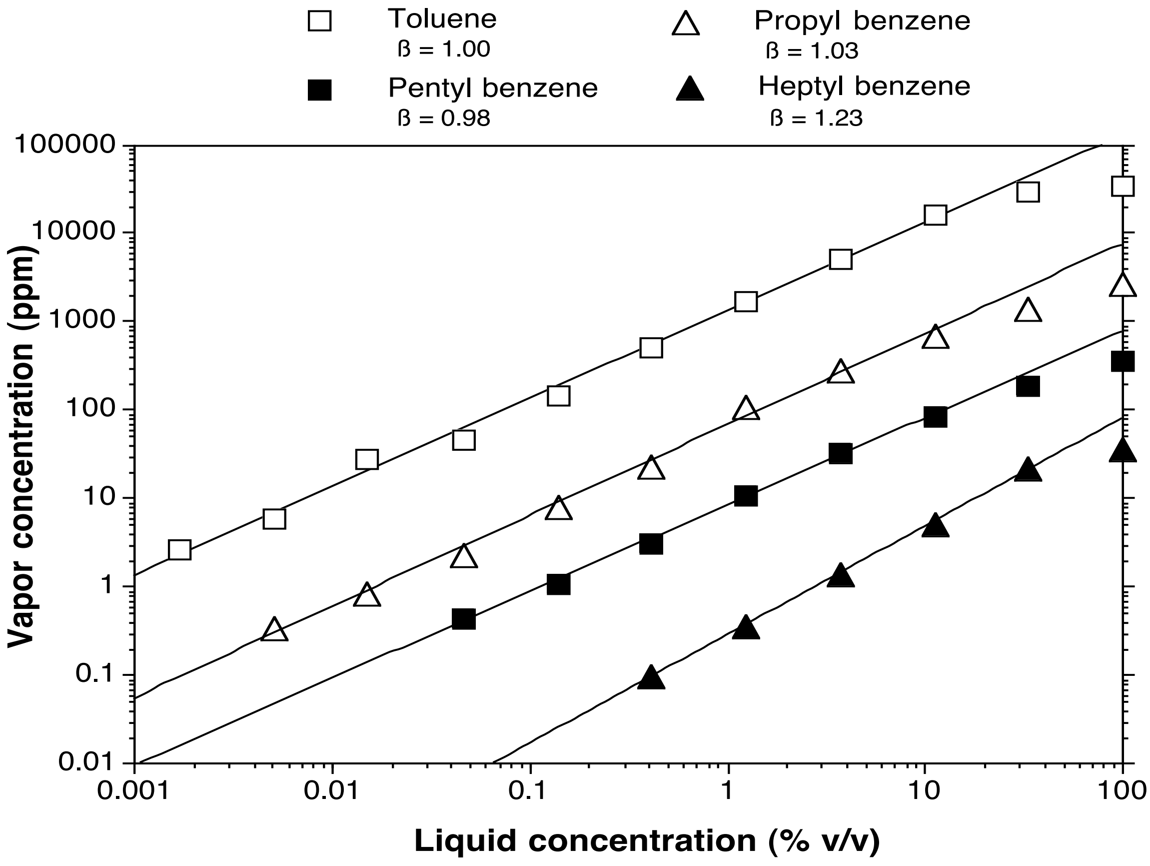


FIGURE 2 e)

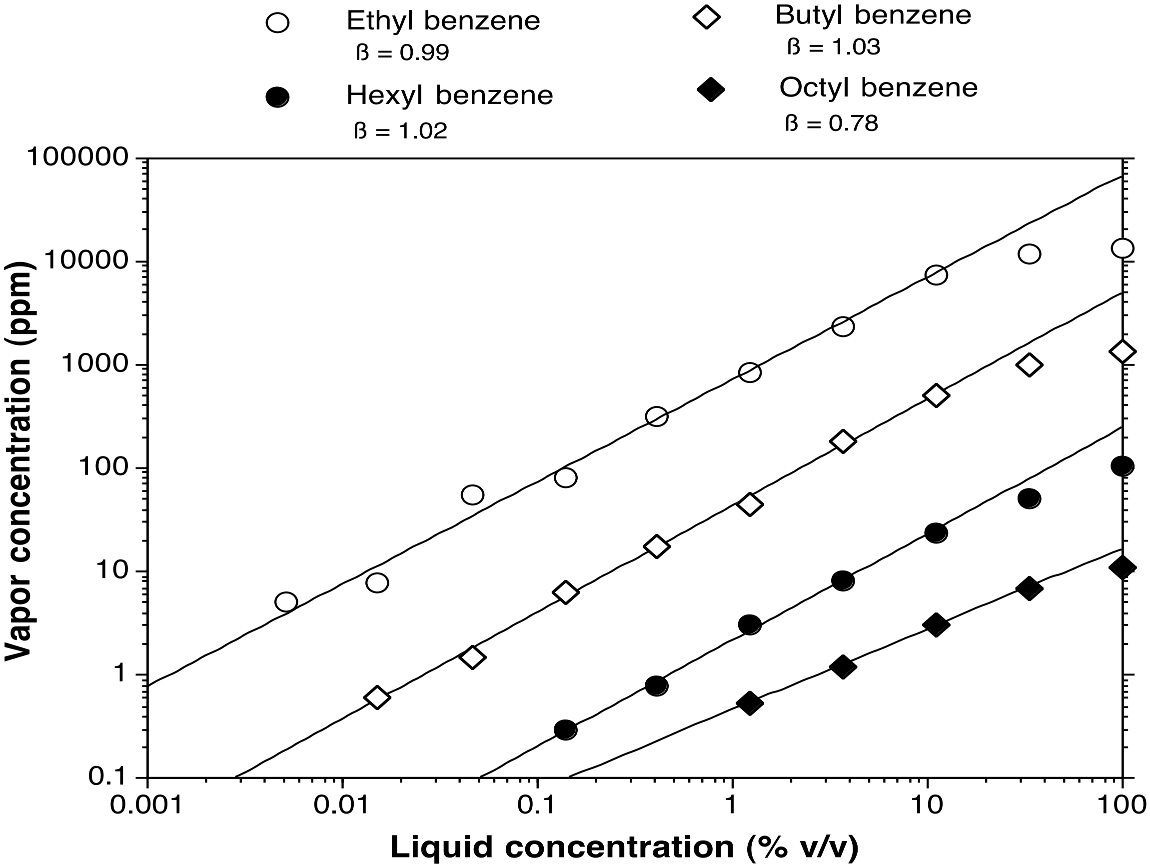


FIGURE 2 f)

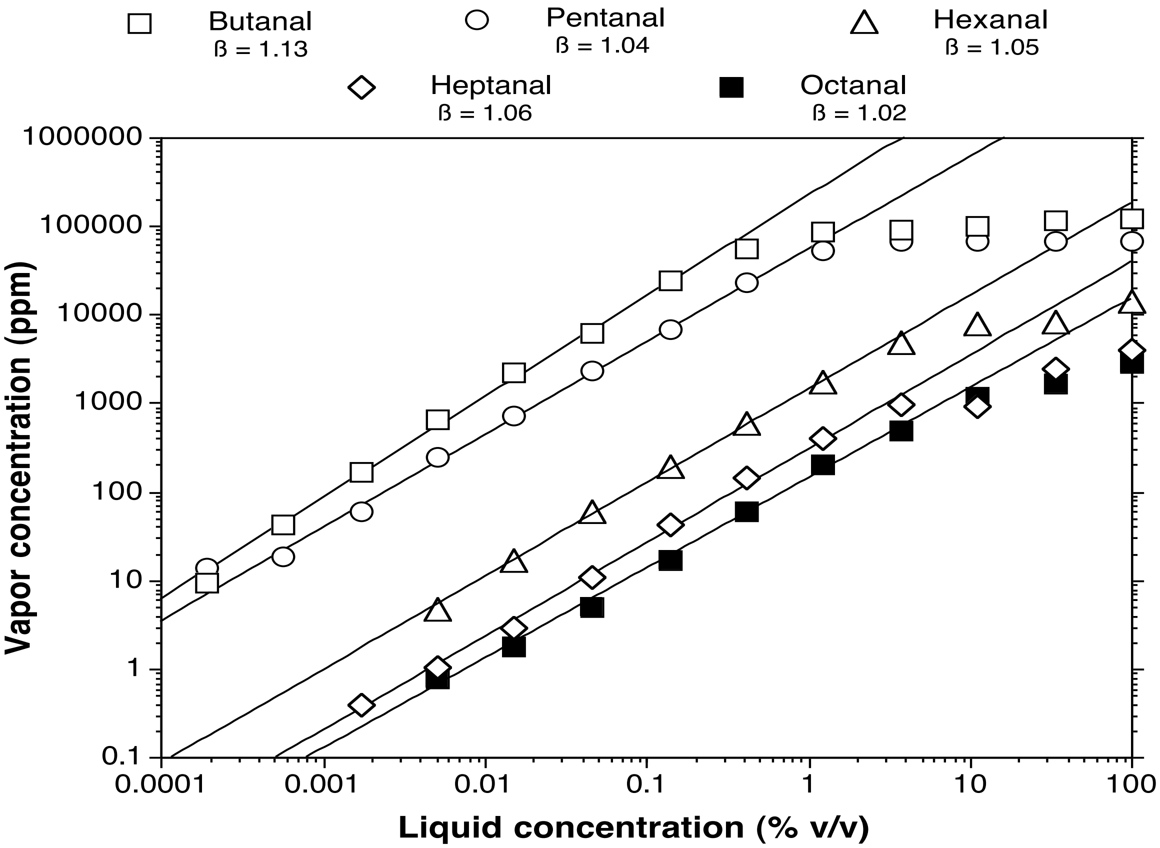


FIGURE 2 g)

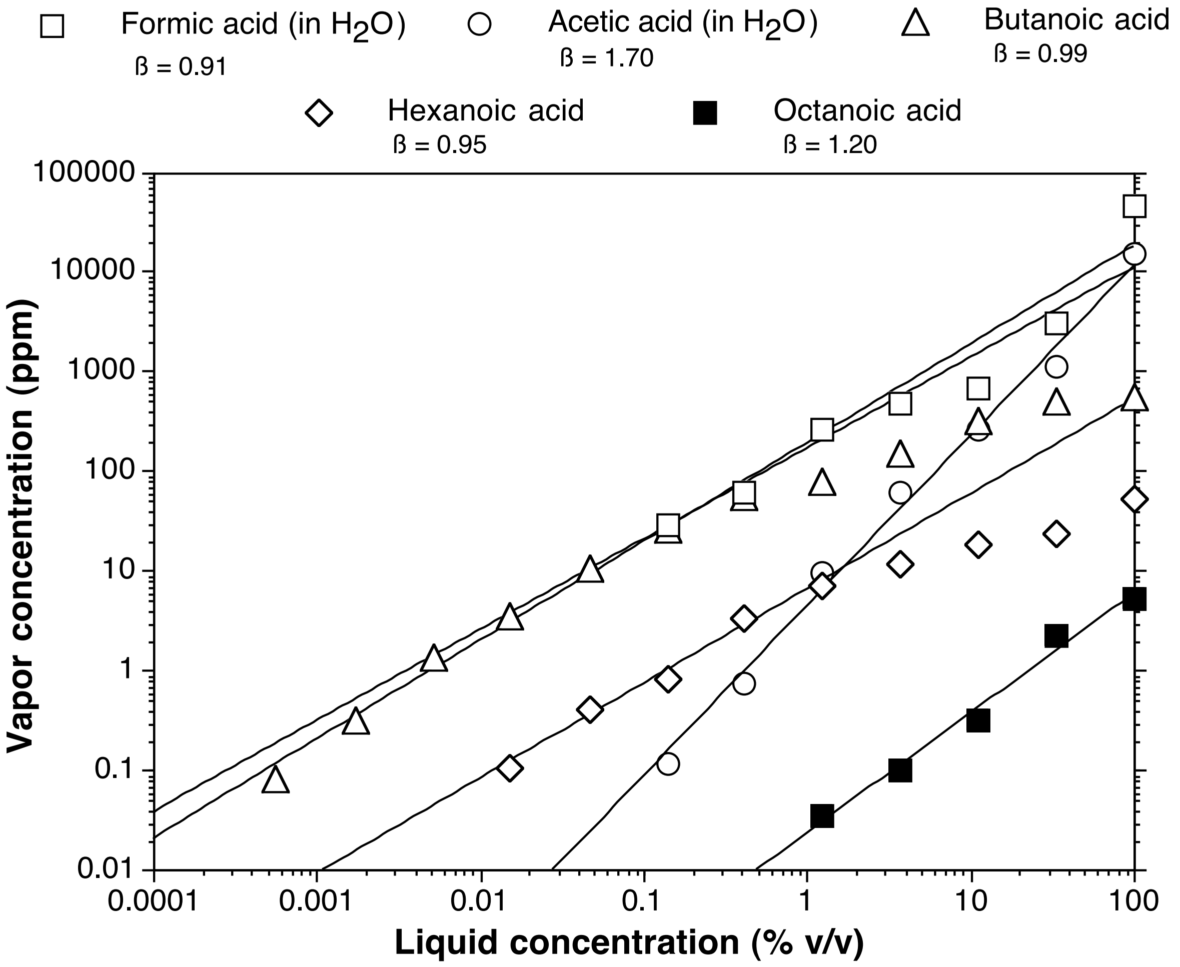

□ Formic acid (in H_2O)
ß = 0.91
○ Acetic acid (in H_2O)
ß = 1.70
△ Butanoic acid
ß = 0.99
◇ Hexanoic acid
ß = 0.95
■ Octanoic acid
ß = 1.20
Vapor concentration (ppm)
100000
10000
1000
100
10
1
0.1
0.01
0.0001
0.001
0.01
0.1
1
10
100
Liquid concentration (% v/v)

FIGURE 3

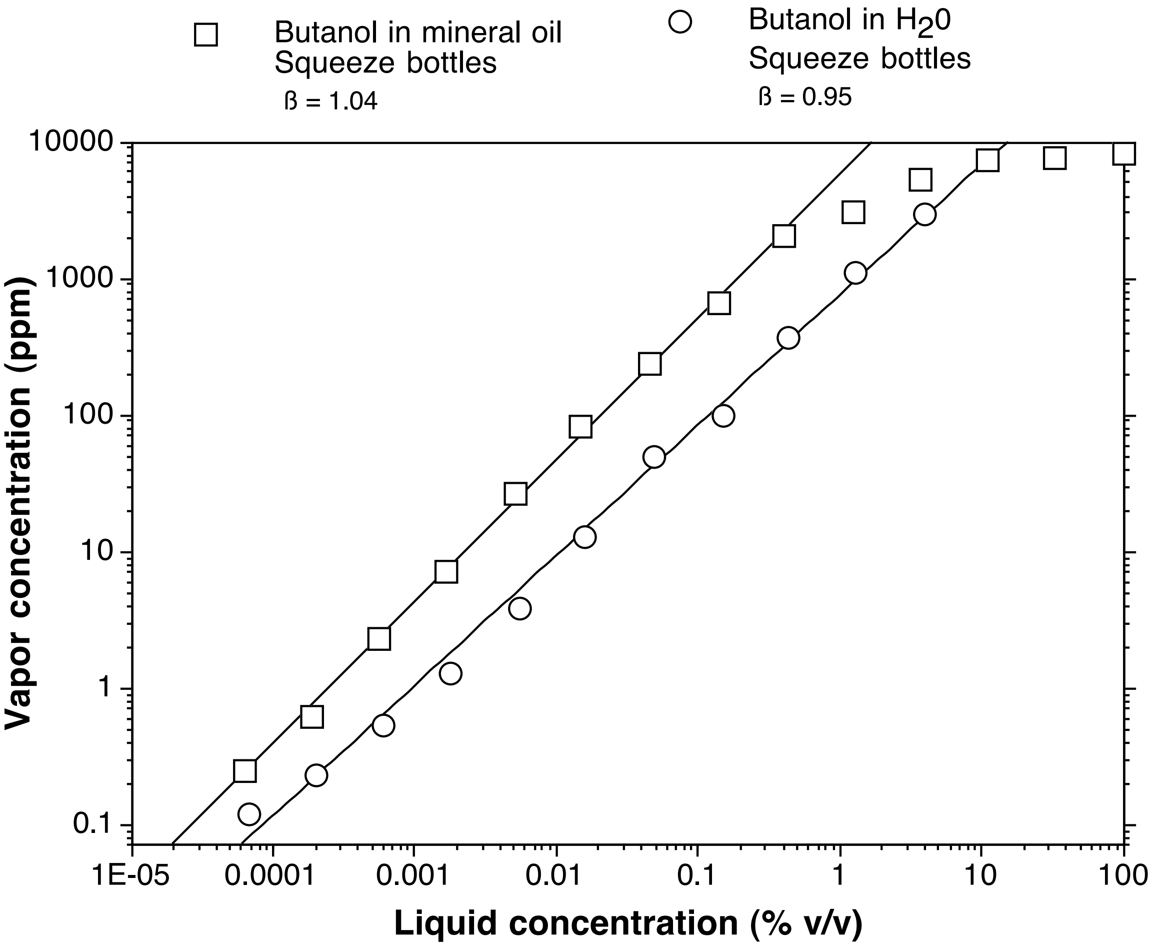

□ Butanol in mineral oil
Squeeze bottles
ß = 1.04
○ Butanol in H_20
Squeeze bottles
ß = 0.95
Vapor concentration (ppm)
10000
1000
100
10
1
0.1
1E-05
0.0001
0.001
0.01
0.1
1
10
100
Liquid concentration (% v/v)

FIGURE 4

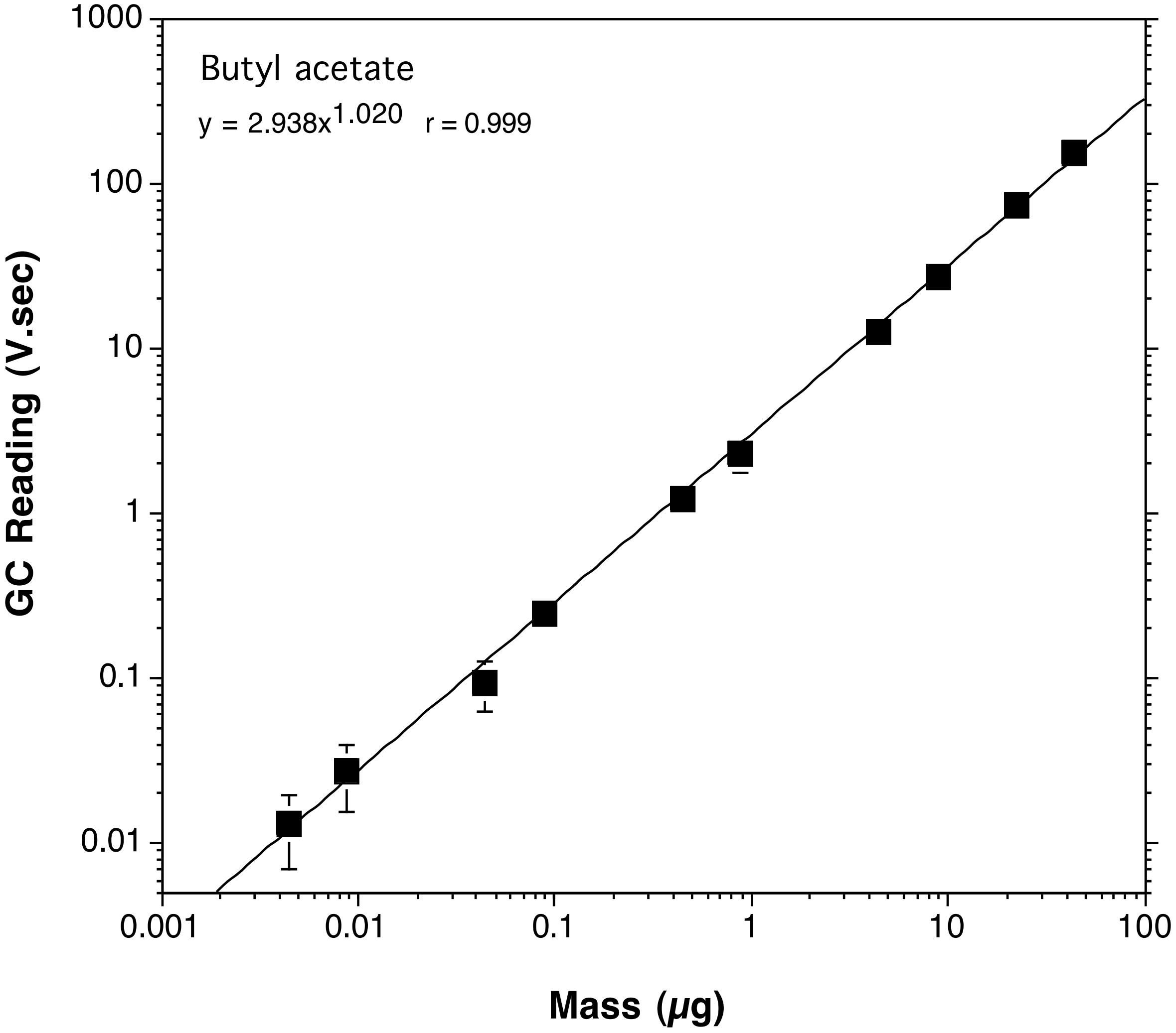

Butyl acetate
y = 2.938x^1.020 r = 0.999
GC Reading (V.sec)
1000
100
10
1
0.1
0.01
0.001
0.01
0.1
1
10
100
Mass (μg)

FIGURE 5 a)

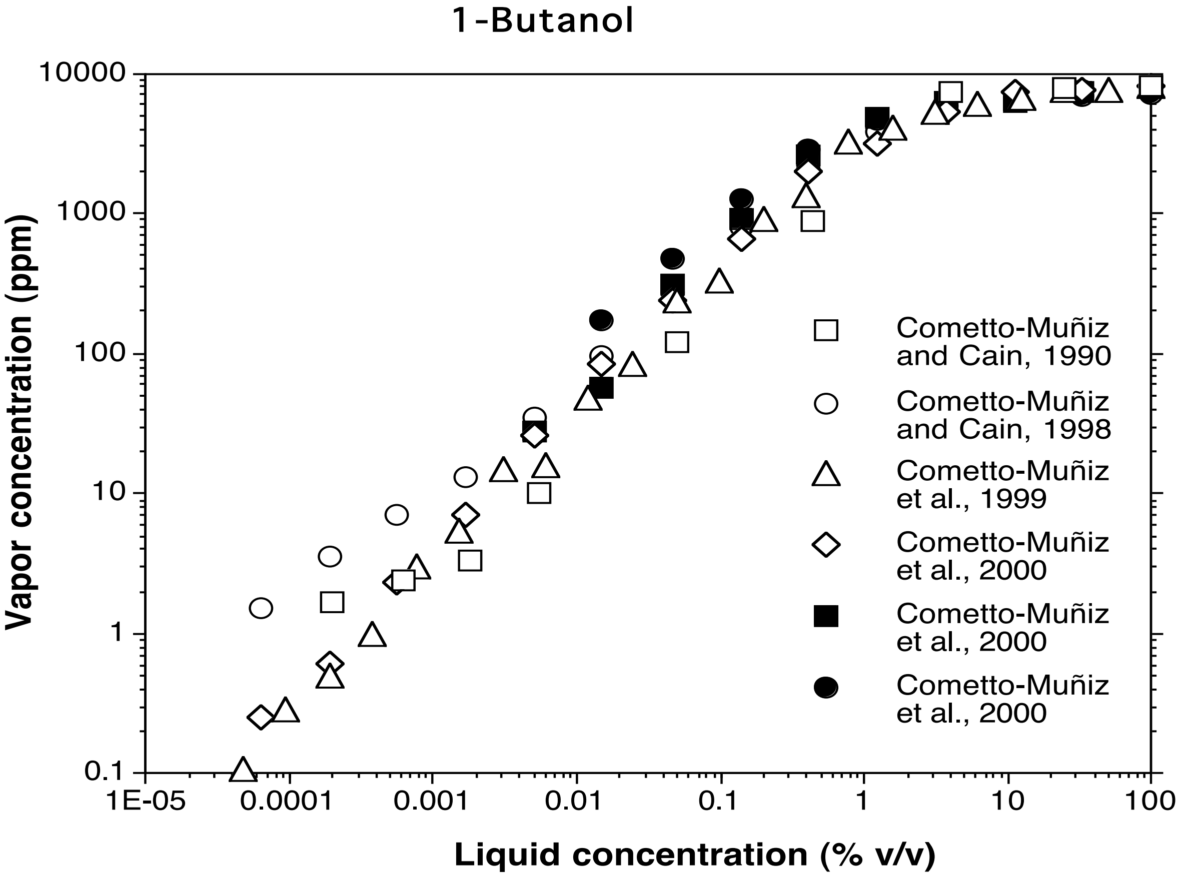


FIGURE 5 b)

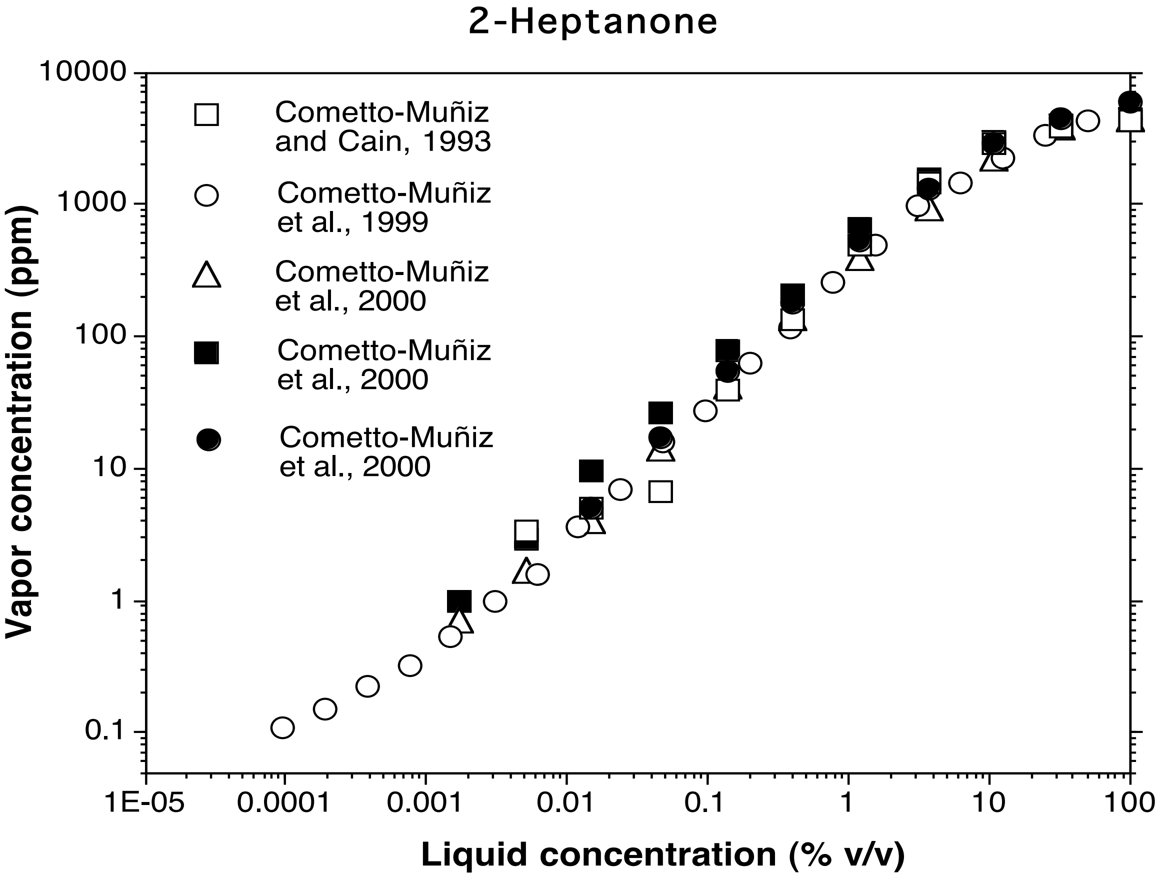
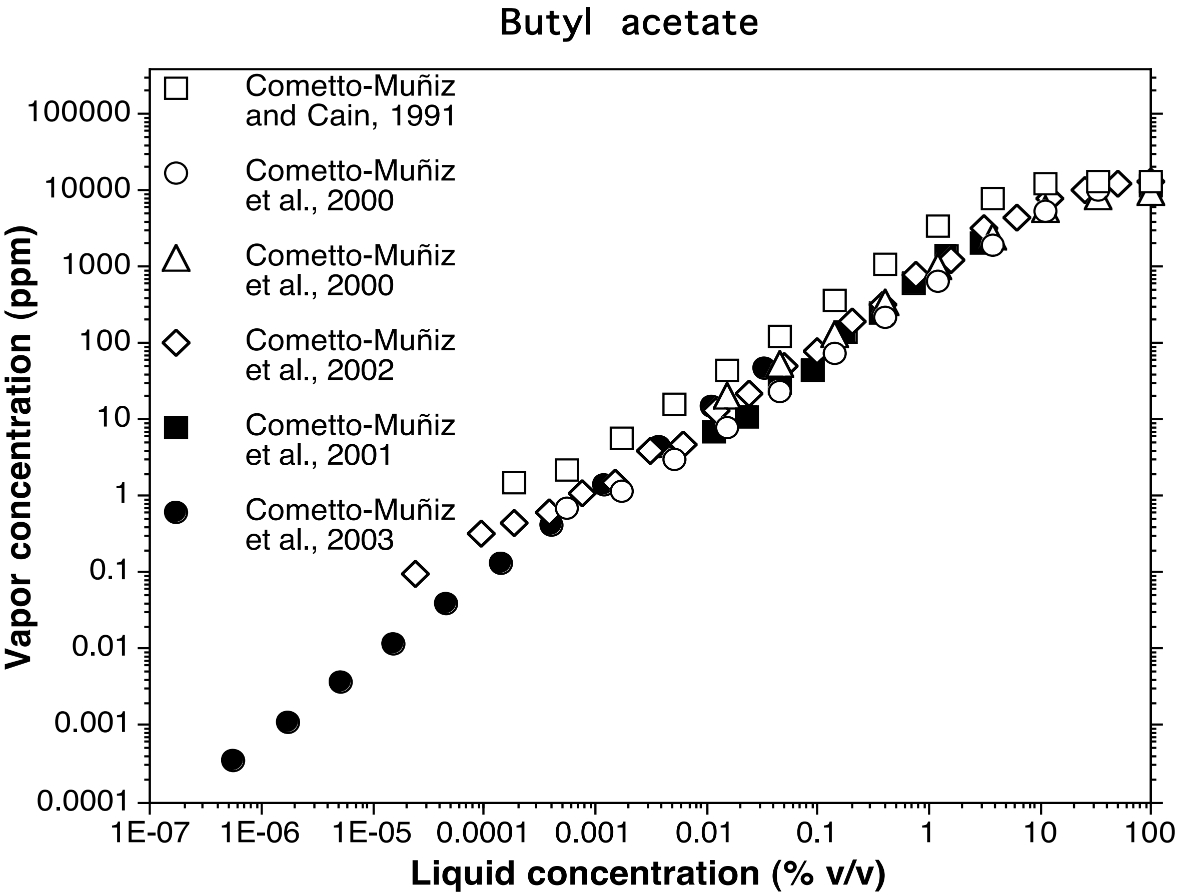
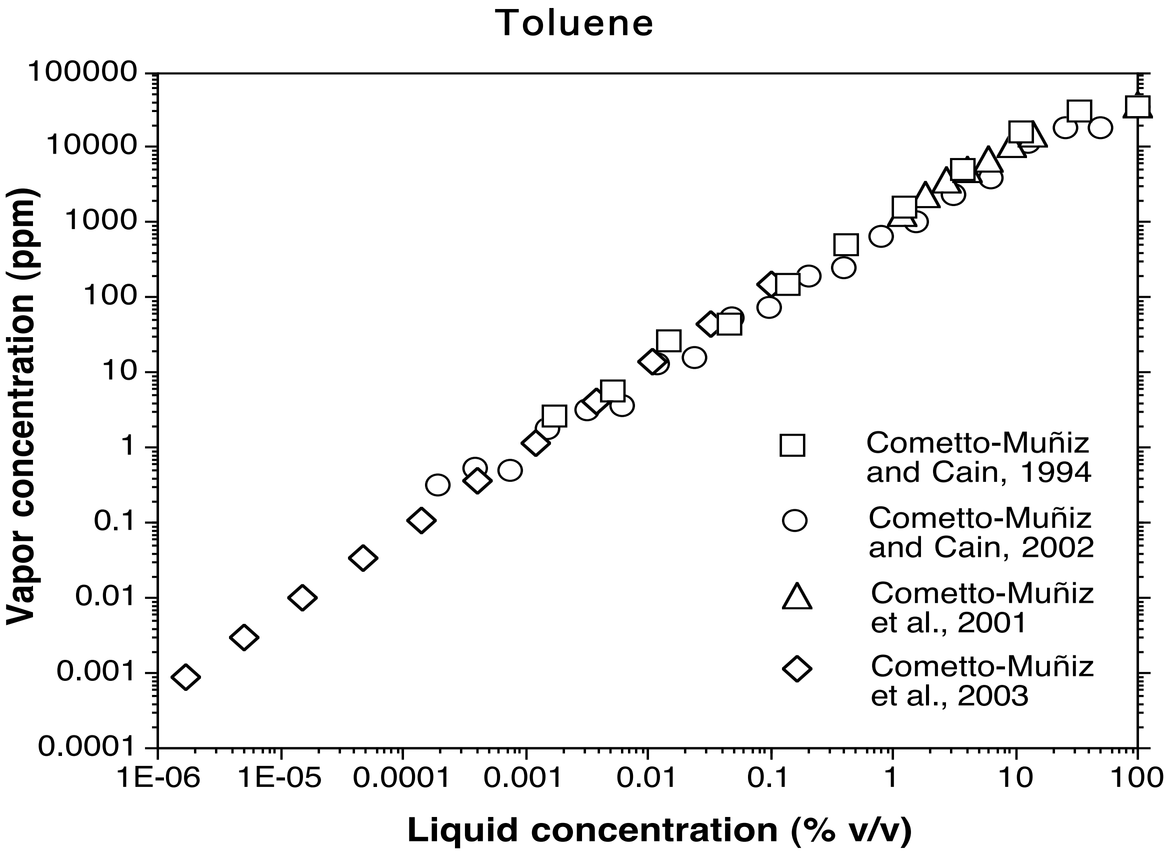


FIGURE 5 c)



Butyl acetate

FIGURE 5 d)



Toluene

FIGURE 6 a)

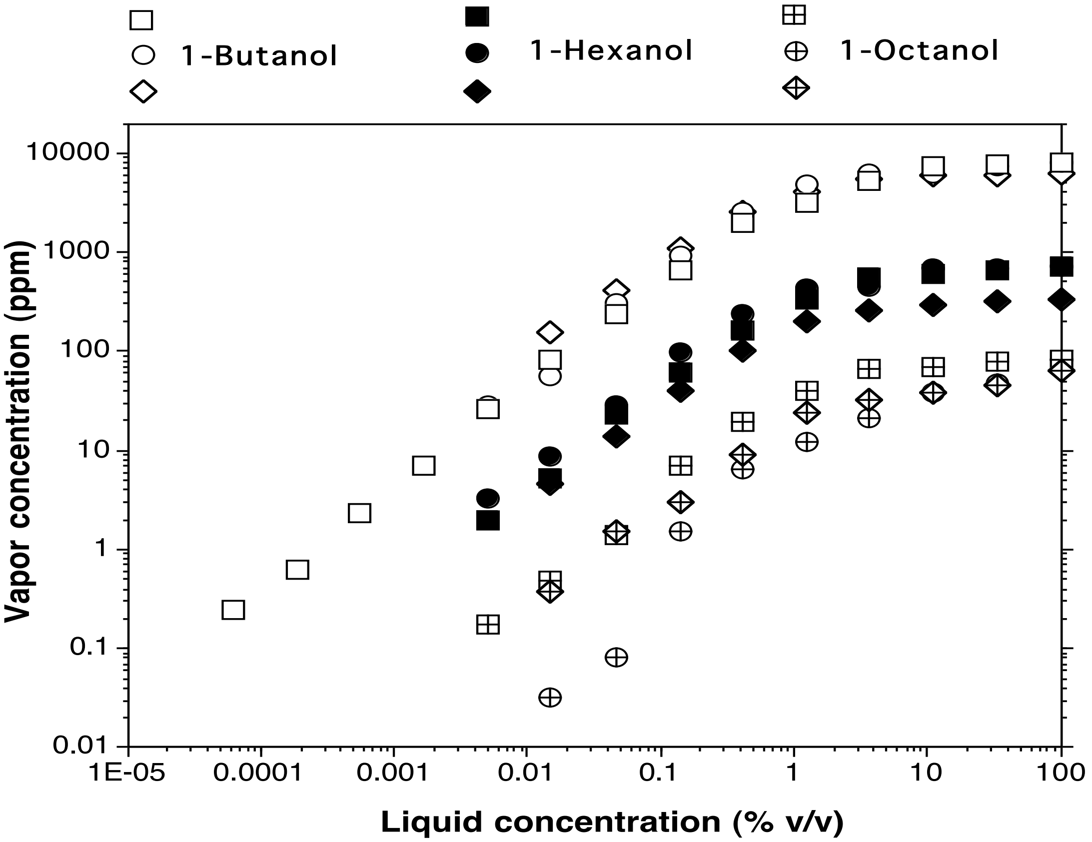


FIGURE 6 b)

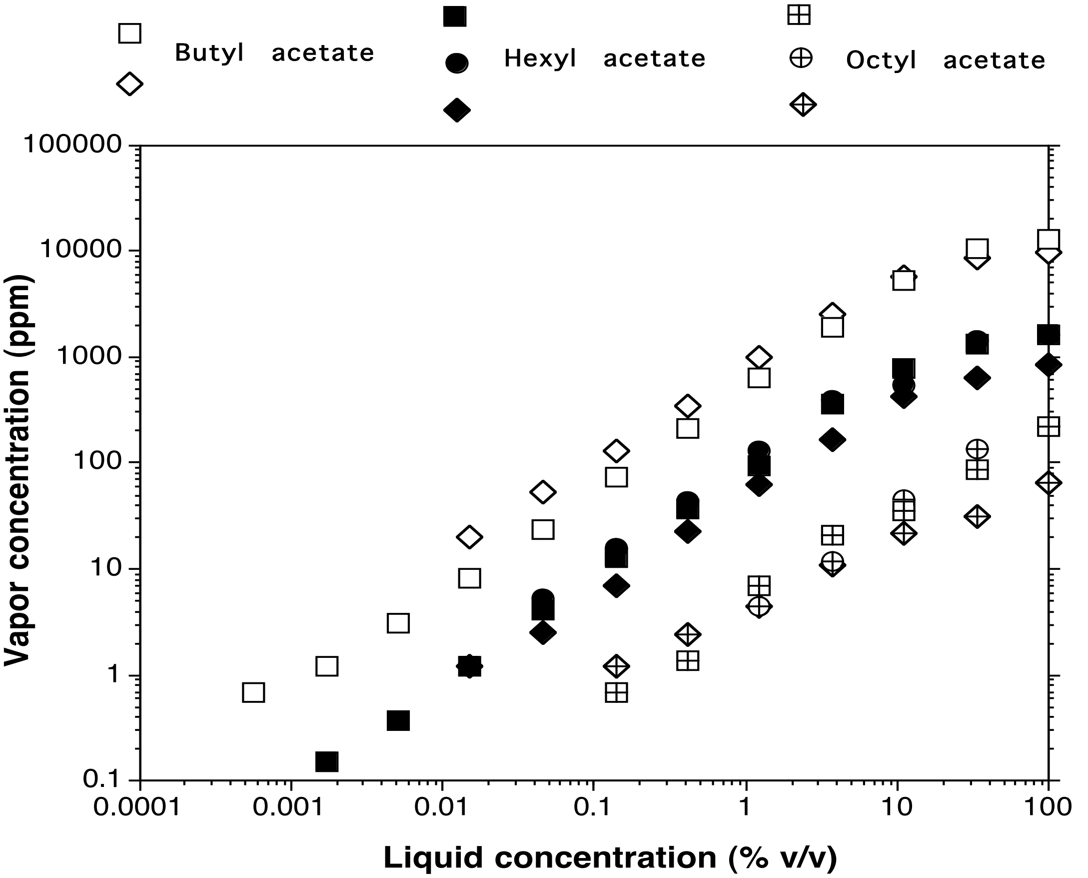
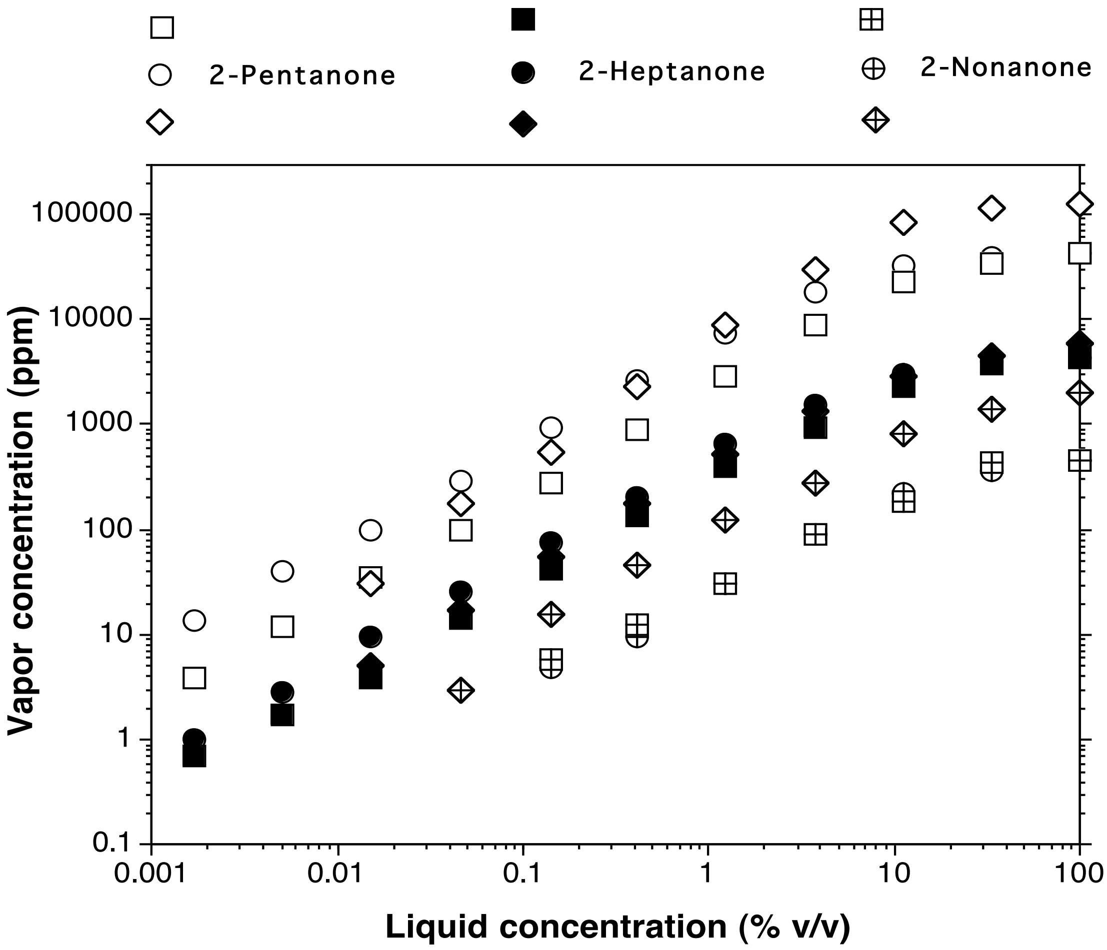


FIGURE 6 c)


□ ○ ◇ 2-Pentanone
■ ● ◆ 2-Heptanone
⊞ ⊕ ◈ 2-Nonanone
Vapor concentration (ppm)
100000
10000
1000
100
10
1
0.1
0.001
0.01
0.1
1
10
100
Liquid concentration (% v/v)