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An assessment of air quality reflecting the chemosensory irritation impact of mixtures of volatile organic compounds

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ABSTRACT

We present a method to assess the air quality of an environment based on the chemosensory irritation impact of mixtures of volatile organic compounds (VOCs) present in such environment. We begin by approximating the sigmoid function that characterizes psychometric plots of probability of irritation detection (Q) versus VOC vapor concentration to a linear function. First, we apply an established equation that correlates and predicts human sensory irritation thresholds (SIT) (i.e., nasal and eye irritation) based on the transfer of the VOC from the gas phase to biophases, e.g., nasal mucus and tear film. Second, we expand the equation to include other biological data (e.g., odor detection thresholds) and to include further VOCs that act mainly by "specific" effects rather than by transfer (i.e., "physical") effects as defined in the article. Then we show that, for 72 VOCs in common, Q values based on our calculated SITs are consistent with the Threshold Limit Values (TLVs) listed for those same VOCs on the basis of sensory irritation by the American Conference of Governmental Industrial Hygienists (ACGIH). Third, we set two equations to calculate the probability (Qmix) that a given air sample containing a number of VOCs could elicit chemosensory irritation: one equation based on response addition (Qmix scale: 0.00 to 1.00) and the other based on dose addition (1000*Qmix scale: 0 to 2000). We further validate the applicability of our air quality assessment method by showing that both Qmix scales provide values consistent with the expected sensory irritation burden from VOC mixtures present in a wide variety of indoor and outdoor environments as reported on field studies in the literature. These scales take into account both the concentration of VOCs at a particular site and the propensity of the VOCs to evoke sensory irritation.

1. Introduction

A number of methods have been used to quantify the sensory irritation of volatile organic compounds, VOCs. The best known method is probably the 'mouse assay' of Alarie, that uses upper respiratory tract irritation in mice to define an RD_{50} value, the vapor concentration of a VOC in ppm that leads to a 50% reduction in the rate of breathing of a mouse (Alarie, 1966, 1973). In turn, the Threshold Limit Values, TLVs, established by ACGIH (ACGIH, 2008) are based on a review of existing published and peer-review literature in various scientific disciplines (e.g., industrial hygiene, toxicology, occupational medicine, and epidemiology) and provide a source of sensory irritation in occupational settings. Recommendations for the establishment of LOAEL (lowest observed adverse effect level on humans) from RD_{50} values have been set out (Kuwabara et al., 2007), as well as NOAEL (no-observed-adverse effect level on humans), again from RD_{50} values (Nielsen et al., 2007). Other quantitative assessments include odor detection thresholds in humans, ODTs, (Devos et al., 1990; Environmental Protection Agency (US EPA), 1992; van Gemert, 2003; Nagata, 2003; Cometto-Muñiz, 2001b) as well as nasal pungency thresholds, NPTs, and eye irritation thresholds, EITs, in humans (Cometto-Muñiz, 2001b). It has recently been proposed (Jakubowski and Czerczak, 2010) that an equation for the prediction of NPTs (Abraham et al., 2001) could be used to predict occupational exposure limits of VOCs.

The above methods of quantification of the sensory irritation effects of VOCs refer to the effects of individual VOCs. Several studies of sensory irritation thresholds (NPTs and EITs) from mixtures of VOCs have shown various levels of additivity that, to a first approximation, are not-too-far from complete additivity (Nielsen et al., 1988; Cometto-Muñiz et al., 1997, 1999, 2001a, 2004a, 2004b). So are results from studies on ODTs (Cometto-Muñiz et al., 2003, 2005b; Wise et al., 2007; Miyazawa et al., 2009). To extend occupational exposure limits to mixtures of VOCs, additivity of effects has been suggested (Alarie et al., 1996). However, there appears to be no application of the additivity of sensory irritation effects to any assessment of the overall air quality due to mixtures of VOCs. It is the aim of this paper to set out such an assessment.

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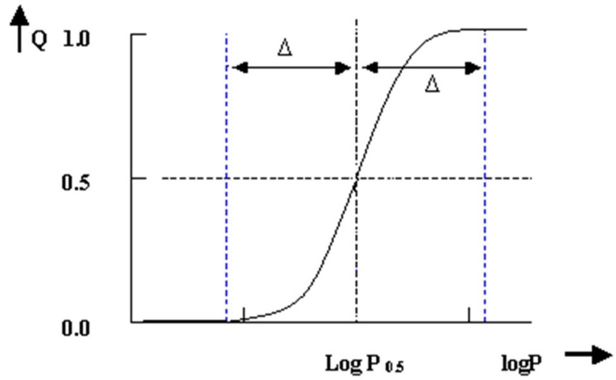

Fig. 1. Typical shape of a psychometric plot of detection probability of a VOC by sensory irritation against its vapor concentration.

2. Methods

2.1. The psychometric plots

We start with the psychometric plots obtained from the probability of sensory irritation detection, Q, of a given VOC as a function of its gaseous concentration, log P with P in ppm (Cometto-Muñiz et al., 1999, 2001a, 2002, 2004a, 2004b, 2007b, 2008c; Cometto-Muñiz and Abraham, 2008a, 2008b; Cain et al., 2006). As for the determination of thresholds, this involves a panel of human subjects. The outcome, for a given VOC, is a probability-concentration plot known as a psychometric plot. The general shape of such a plot is shown in Fig. 1, where Q is the probability of detection corrected for chance (Macmillan and Creelman, 1991). For sensory irritation, the plot is extraordinarily steep, and the difference in log P corresponding to chance detection, Q = 0, and perfect detection, Q = 1, is typically around one log unit, e.g. (Cometto-Muñiz et al., 2002, 2004b). This is indicated on the plot by Δ, where 2Δ = one log unit in log P. The log P value corresponding to Q = 0.5, is that of the detection threshold, shown as log $P_{0.5}$.

These psychometric plots are very important indeed. The probability of detecting a VOC tails off to zero within a relatively narrow concentration range as log P becomes progressively smaller. Below a gaseous concentration of (log $P_{0.5}$–Δ), the probability of detecting a VOC is zero. Since Δ = 0.5 log units only, the probability decreases to zero quite sharply.

A second very important finding is that of a cut-off effect. On ascending a homologous series of VOCs, the potency of a VOC increases as shown in Table 1.

What is evident (Cometto-Muñiz et al., 1998b, 2005a, 2005c, 2006, 2007a, 2007b, 2010; Cometto-Muñiz and Abraham, 2008b; Cain et al., 2006) is that this increase in sensory irritation potency does not simply carry on along a homologous series, but a homolog is reached where the potency declines to zero. For each of the alcohols in Table 1, as the gaseous concentration of alcohol is increased, Q in the psychometric plots approaches unity. But Q for decan-1-ol never reaches beyond 0.5 no matter what is the gaseous concentration, and the same happens for undecan-1-ol (Cometto-Muñiz et al., 2005a, 2007b). For still higher homologs the maximum value of Q will be around zero. For the carboxylic acids, Q for hexanoic acid reaches values greater than zero, but Q for heptanoic and octanoic acids are definitely near zero (Cometto-Muñiz et al., 2005c, 2007a). This cut-off effect has been found in all the homologous series studied (Cometto-Muñiz, 2001b; Cometto-Muñiz et al., 2010). It looks like the sensory irritation receptive system is very broad in that it will accept almost any VOC, unless the VOC exceeds a critical size that allows it to interact effectively with the relevant receptors. One measure of 'size' is the VOC descriptor, *L* (the gas-hexadecane partition coefficient at 25 °C, see later), and it is useful to compare the *L*-values at the cut-off points for various series, see Table 2 (Cometto-Muñiz et al., 2005a, 2006, 2007a, 2007b). It seems that any VOC with an *L*-value more than about 6.1 will not be effective in eliciting sensory irritation.

Table 1
Some EIT values (from Abraham et al., 2003).

VOC	Log(1/EIT)
Ethanol	−4.76
Propan-1-ol	−3.74
Butan-1-ol	−3.37
Hexan-1-ol	−2.60

Table 2
Values of *L* at various cut-off points along homologous series.

VOC	*L*
Undecan-1-ol	6.13
Decyl acetate	6.24
Heptanoic acid	4.18
Heptyl benzene	6.22
Tridecanone	6.67
Dodecanal	6.31

The psychometric plots can be fitted to sigmoid type functions, but this is not very helpful, because the constants for the function vary from VOC to VOC and in any case are known only for a limited number of VOCs. Advantage can be taken of the fact that Δ in Fig. 1 does not vary very much with the VOC—what varies appreciably is the position of the curve along the log P axis. This is defined by the detection threshold for the VOC, which corresponds to the point shown as Q = 0.5 and log P = log $P_{0.5}$.

An approximation to the psychometric curve is shown in Fig. 2. The full line is given by Eq. (1), where SIT is the sensory irritation threshold.

$$Q = 0.5 + [\log P/\mathrm{ppm} - \log \mathrm{SIT}] \quad (1)$$

A point to consider is that Eq. (1) will yield negative values of Q when the gaseous concentration is less than (log $P_{0.5}$ − Δ), i.e. less than (log SIT − 0.5). However this can easily be overcome by setting Q = 0 for log P < (log SIT − 0.5). In addition, one can set Q = 1 for log P > (log SIT + 0.5), leading to the approximation shown in Fig. 2.

In order to apply Eq. (1), it is necessary to calculate (predict) the sensory irritation threshold, SIT, for any VOC, as described in the next section.

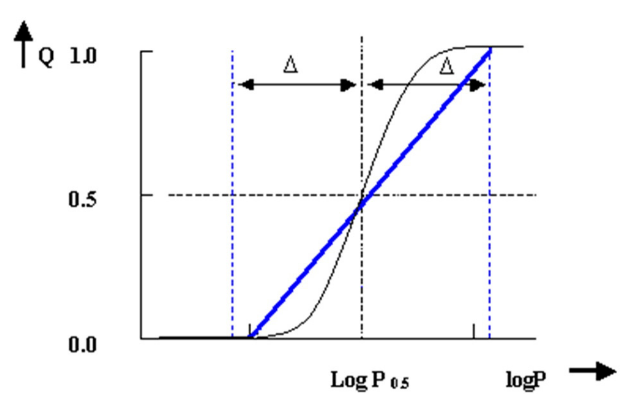

Fig. 2. The approximation to the sensory irritation psychometric plot.