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Comparison of odor detection thresholds and odor discriminablities of a conducting polymer composite electronic nose versus mammalian olfaction

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Abstract

Response data from an array of conducting polymer composite vapor detectors that form an electronic nose were collected for the purpose of comparing selected, quantitatively measurable, phenomena in odor detection and classification to the olfactory characteristics of monkeys and humans. Odor detection thresholds and discriminability between structurally similar pairs of odorants were the two primary quantities evaluated for this comparison. Comparisons were only made for volatile organic vapors as opposed to aroma active odorant vapors. Electronic nose detection thresholds for a homologous series of *n*-alkane and 1-alcohol odorants were determined and the results were compared to literature values for the mean olfactory detection thresholds observed in psychophysical experiments on humans exposed to these same vapors. The trends in odor detection thresholds of the electronic nose towards the tested analytes were very similar to those exhibited by humans. The discrimination performance of the electronic nose for distinguishing between pairs of odorants within incrementally varying series of esters, carboxylic acids and alcohols were also compared to the published data of Laska and co-workers on the psychophysical performance of humans and monkeys for these same odorant pairs. Similar trends were generally observed between the humans, monkeys, and the electronic nose in that discrimination performance increased as the compounds of an odorant pair became more structurally dissimilar. With use of the Fisher linear discriminant algorithm for classification of these test pairs of odorants, the electronic nose exhibited significantly better discriminability than humans or monkeys for the odorant pairs evaluated in this work under the test conditions for which the discriminability was evaluated.

Keywords: Electronic nose; Conducting polymer composites; Odor detection threshold; Odor discriminabilities

1. Introduction

The human olfactory epithelium contains $\approx 10^6$–10^7 total olfactory receptor neurons, which each are thought to contain only one of $\approx 10^3$ different types of olfactory receptor proteins [1–8]. It has been recently shown that one odorant receptor recognizes multiple odorants and that one odorant is recognized by multiple odorant receptors, but that different odorants are recognized by different combinations of odorant receptors [9]. These observations support some previous hypotheses of a distributed olfactory response to odorants as a possible mechanism for detection of odorants by the olfactory system [3–6,10–13]. Broad responsiveness to odorants has also been experimentally observed from electrophysiological recordings in the mammalian olfactory epithelium and in mitral/tufted cells [14].

Several artificial/electronic olfactory systems are being developed based on the notion of using broadly cross-reactive arrays of chemical sensors [15–21]. Such array modalities can include conducting organic polymers, polymer-coated surface acoustic wave resonators, polymer-coated quartz crystal microbalances, conducting polymer composites, dye-impregnated polymers coated on optical fibers, and electrochemical gas sensors [1,15–22]. These systems share the common trait of ''cross-reactivity'', in that a given detector responds to a variety of odorants and that a given odorant elicits a response from a variety of detectors. Pattern recognition algorithms are then used to classify and quantify odorants based on the data stream produced by the detector array. The gross behavior of such systems therefore resembles mammalian olfaction in that the system need not be designed in advance to detect a particular odorant. Instead, the systems can

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learn new patterns and can associate these patterns with new odorants through use of training and data storage functions.

The particular electronic nose implementation evaluated in this work is comprised of an array of conducting polymer composite vapor detectors [23,24]. Each detector is a chemically-sensitive thin film that undergoes a change in electrical resistance upon exposure to a vapor. The resistors are made from composites having regions of an electrical conductor (typically carbon black, although other conductors can also be used) interspersed into regions of an insulating organic material, typically an organic polymer. Sorption of an odorant into the polymer causes a swelling of the film, which decreases the connectivity between the regions that comprise the conducting phase of the composite. This change in connectivity modifies the electrical resistance of the detector. Removal of the stimulus leads to desorption of the odorant and a decrease in resistance back to the original baseline response value. Different polymers display different gas/polymer sorption constants so that the signals obtained from an array of detectors, each made of a compositionally different conductor/insulator composite, provide a fingerprint that can be used for identification, classification, and quantification of odorants. This particular electronic nose array implementation is advantageous because the polymers that can be used in the detectors can vary widely in their chemical and physical properties. A wide range of odorants can therefore be discriminated based on the response patterns that the odorants produce on the sensor array [23,24]. In addition, electrical resistance is an easily measured experimental quantity, and the steady state signal response signals for odorants tested to date are linearly dependent on the concentration of analyte in the gas phase above the detector [23,25]. This combination of features allows for a very simple algorithmic implementation to obtain robust odor classification and quantification under a variety of ambient conditions.

Some of the questions of interest in these artificial systems relate to how their performance, on a system-level basis, compares to that of mammalian olfaction. To make this comparison, in this work we specifically addressed how well the electronic nose, as compared to humans and monkeys, can discriminate between selected pairs of odorants. In addition, we have determined odor intensity thresholds for the current (highly unoptimized) version of the conducting polymer composite electronic nose, in order to evaluate trends in detection limits of humans relative to the detection capabilities of the electronic nose. Comparisons were only made for volatile organic vapors as opposed to aroma active odorants. These discrimination and odor sensitivity data are interesting in their own right but additionally are of importance in benchmarking the status of the electronic nose towards the long-range goal of constructing an artificial/electronic system that functionally mimics the human sense of olfaction.

2. Experimental

An automated system consisting of LabVIEW software, a Pentium computer, a Keithley channel switcher, a Keithley multimeter, and electronically-controlled solenoid valves and mass flow controllers, was used to deliver selected concentrations of solvent vapors to the detectors in the electronic nose array. The system was also used to monitor the resistance of the detectors. The apparatus has been described in detail previously [23]. The analytes were purchased from Aldrich and Pfaltz & Bauer.

To obtain the desired analyte concentration, a stream of carrier gas was passed through a bubbler that had been filled with the solvent of choice. The carrier gas for all experiments was oil-free air, obtained from the general compressed air laboratory source, containing 1.10 ± 0.15 ppth (parts per thousand) of water vapor. The air was filtered to remove particulates, but deliberately was not dehumidified nor otherwise purified. Fluctuations in laboratory temperature, $21.5 \pm 1.5^{\circ}$C, could cause a $\sim$10% error in setting and controlling the vapor concentrations between nominally identical exposures over the course of the data collection analyzed in this work. No temperature control of the apparatus or of the carbon black-polymer composite detectors was performed. Saturation of the carrier gas with the solvent vapor was verified through measurement of the rate of mass loss of the solvent in the bubbler. The mass flow controllers were verified independently to be within specification prior to and after an experimental run. In addition, calibrations of the flow system using a flame ionization detector (FID) (Model 300 HFID, California Analytical Instruments, Inc.) verified that the analyte concentrations actually delivered to the sensors were those expected from the settings of the mass flow controllers. The flame ionization detector was calibrated using toluene/air standard calibration gas mixtures sold by Scott Specialty Gases, Inc. Corrections were made for the sensitivity changes of the FID unit for toluene versus other gases when determining the concentrations of the other analytes of interest in this work.

Detector fabrication methods have been described in detail in the literature. [23,24]. All detectors evaluated in this work were made from composites of carbon black with insulating organic polymers. The detector array used in determining the electronic nose detection thresholds for the homologous series of *n*-alkane (*n*-pentane, *n*-hexane, *n*-heptane, *n*-octane and *n*-nonane) and 1-alcohol (methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol) odorants consisted of 20 conducting polymer composite detectors. Two detector copies were made from each of the 10 polymers listed in Table 1 (purchased from Aldrich and Polysciences). The polymers were chosen to encompass a broad range of chemical properties, but were selected with no specific knowledge of how well the detectors would perform for the odor discrimination tasks of concern in this study. Each detector was fabricated by spin-coating mixtures containing a dissolved polymer and suspended carbon

Table 1
Polymers contained in the detectors of the electronic nose arrays

Detector	Polymer
1	Poly(4-vinyl phenol)
2	Poly(*N*-vinyl pyrrolidone)
3	Poly(sulfone)
4	Poly(methyl methacrylate)
5	Poly(caprolactone)
6	Poly(ethylene-*co*-vinyl acetate), 82% ethylene
7	Poly(ethylene oxide)
8	Poly(ethylene)
9	Poly(vinylidene fluoride)
10	Poly(ethylene glycol)

black particles onto a glass slide, as described previously [23,24].

A second detector array, made from the same polymers and using the same fabrication techniques, was used to test the ability of the electronic nose to discriminate pairwise between various odorants within series of esters (isopentyl acetate, isopentyl propionate, isopentyl butanoate, isopentyl pentanoate, isopentyl hexanoate, ethyl acetate, *n*-propyl acetate, *n*-butyl acetate, *n*-pentyl acetate, *n*-hexyl acetate, *n*-octyl acetate, *n*-decyl acetate, isopropyl acetate and isobutyl acetate), alcohols (ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 2-pentanol and 3-pentanol) and carboxylic acids (*n*-propanoic acid, *n*-butanoic acid, *n*-pentanoic acid, *n*-hexanoic acid, *n*-heptanoic acid, isobutanoic acid, isopentanoic acid and isohexanoic acid).

For detection threshold measurements, the the detector response was taken as the difference between the baseline resistance and the maximum resistance observed during the 10 min exposure to the odorant-containing air flow. This 10 min odorant exposure was always preceded by, and followed by, a 2 min exposure to a flow of air that was obtained from the general laboratory source. The resistance values were measured with a Keithley Model 2002 multimeter by integrating over a measurement aperture of 167 ms. Detection thresholds were defined as the lowest concentration at which any detector in the electronic nose array had a response with a signal to noise (s/n) ratio of 3. Thus, at the detection threshold an odorant could be detected but would generally not be identifiable without use of a sophisticated signal processing algorithm, due to the lack of significant responses from multiple detectors at the S/N level of 3:1. This definition of the detection threshold was employed previously in a study of surface acoustic wave-based vapor detectors [26]. The noise of a given detector was defined as the standard deviation in the residuals about a nine-point moving average of the baseline resistance values, spanning approximately 35 s. Using conventional procedures as described in analytical chemistry textbooks [27], the expected detection thresholds were then estimated based on the noise levels typical of the better detectors (i.e. slightly less than 10 ppm for the detectors containing poly(ethylene oxide), poly(ethylene) and poly(ethylene glycol), which had baseline resistances of approximately 1.3×10^4, 1.2×10^4 and $4.0 \times 10^3\ \Omega$, respectively over the course of the experiment) in combination with the knowledge of the signal amplitude at a known, relatively high concentration of odorant, and prior reports that the steady state detector response values generally vary linearly as a function of odorant concentration [23,25,28]. To verify these detection level estimates, each of the 10 odorants was then delivered, at three separate concentrations which generall spanned approximately an order of magnitude near the expected detection threshold. For each odorant, the largest signal to noise ratio of any of the detectors, at the lowest concentration where a signal was detected, was used to determine the detection threshold by linearly extrapolating down to a signal to noise ratio of 3. The extrapolations were never larger than a factor of 5 and were typically less than a factor of 3.

For quantifying odor discrimination, the electronic nose was exposed 10 times to each of the odorants to be discriminated. The order was randomized within subsets of a maximum of eight odorants, because the automated odorant delivery apparatus could handle only eight odorants at a time. The experimental protocol for each exposure was 5 min of clean air flow, followed by 5 min of air flow containing the odorant at a partial pressure corresponding to 1% of its vapor pressure, followed by another 5 min of clean air flow. Only the steady state signal response of the detectors was used in evaluating the discrimination capability of the electronic nose. Use of these values reflects only the relative partition coefficients of the analytes into the various polymer films of the detectors, and does not utilize kinetic sorption information in classifying odorants. In addition, use of the steady state response value largely eliminates variation in response properties due to fabrication-related parameters such as inhomogenieties in detector film thickness and/or variability in the loading of the carbon black particles in the polymeric detector films [28]. The time required to reach this steady state response value depended on the type of polymer and type of analyte, and on the thickness of each polymer in the detector array. In addition, in the most rapidly responding cases the response time depended on the mass transport properties of analyte from the bubbler source through the delivery system to the vicinity of the detectors. Response times for many detectors were below 5 s, although some polymer/analyte combinations required longer times to reach their steady state values. The steady state response data were processed to extract the relative differential resistance response signals, as described previously [23–25] upon exposure to the test vapors of interest.

The pairwise odor discrimination performance of the electronic nose was evaluated using the Fisher linear discriminant algorithm [23–25]. A resolution factor (rf) for any solvent pair can be obtained along any vector, $\vec{w}$, from the vector projection onto $\vec{w}$ of the distance between the cluster

centroids, $d_{\vec{w}}$, divided by the sum of the projected standard deviations, $\sigma_{a,\vec{w}}$, and $\sigma_{b,\vec{w}}$, for data arising from repeated exposures for two different analytes, *a* and *b*. The resulting numerical resolution factor along $\vec{w}$ is defined as

$$\mathrm{rf} = \frac{d_{\vec{w}}}{\sqrt{\sigma^2_{a,\vec{w}} + \sigma^2_{b,\vec{w}}}}$$

The Fisher linear discriminant operates by searching for the vector, $\vec{w}$, such that the rf value is maximized along this optimal discriminant vector. Assuming a Gaussian distribution relative to the mean value of the data points in a given cluster, the probabilities of correctly identifying an analyte as *a* or *b* are approximately 72, 92 and 98% from a single presentation when analytes *a* and *b* are separated with resolution factors of 1.0, 2.0, or 3.0, respectively. Data extracted from multiple exposures of an analyte estimate the statistical distributions of the clustered data.

Because the 20-detector array contained two copies of nominally the same 10-detector array, random combinations of 10-detectors (constrained to each contain exactly one of each of the 10 polymer types) were evaluated to obtain a measure of variability in the ability of a 10-detector electronic nose to discriminate odorants. For each randomly selected 10-detector array, the response signals were normalized and then the Fisher linear discriminant method was used to quantify the ability of the electronic nose to distinguish the odorants [23]. The rf for resolving a given odorant pair was then taken as the mean rf over the results from 10 randomly selected 10-detector arrays.

3. Results and discussion

3.1. Determination of detection thresholds for the electronic nose and comparison with human olfactory threshold levels

3.1.1. Determination of detection thresholds for the electronic nose

The detection thresholds obtained for the electronic nose upon exposure to the homologous series of alkanes (*n*-pentane to *n*-nonane) and alcohols (methanol to 1-pentanol) are shown in Fig. 1a and b. Within each homologous series of odorants, the electronic nose detection threshold values decreased with decreasing vapor pressure of the odorant. This behavior is in accord with prior work, which showed that lower vapor pressure odorants have larger mean partition coefficients for sorption into polymer composite detector films [29]. In the case of the homologous series of *n*-alkanes, detectors containing poly(ethylene oxide) and poly(ethylene) exhibited similar signal to noise ratios and were the detectors that defined the detection threshold of the array towards these odorants. In contrast, a poly(ethylene glycol)-based detector exhibited the largest signal to noise ratios for methanol, ethanol and 1-propanol while a

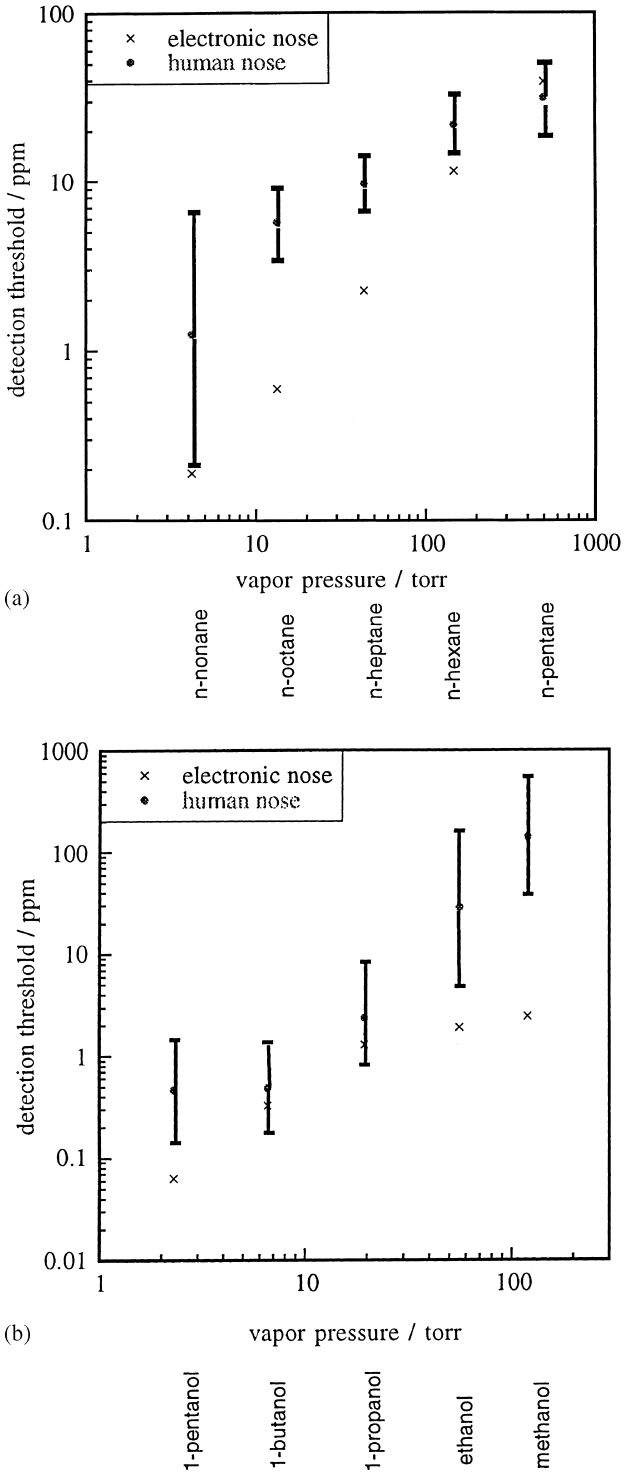


Fig. 1. Plots of the detection threshold in parts per million (ppm) of odorant in air, for the average human [30] and the electronic nose, vs. odorant vapor pressure for homologous series of (a) alkanes from *n*-pentane through *n*-nonane and (b) alcohols from methanol through 1-pentanol. The detection threshold data for humans are mean values for many humans and also are averaged over the results of many investigators as reported in the literature. Estimates of the standard deviations of the reported mean detection values for a given odorant are shown. The standard deviations for a particular set of electronic nose detectors upon repeated exposures to a given concentration of analyte are approximately the height of the "X" symbols depicted in the figures.

poly(ethylene oxide)-based detector exhibited the largest signal to noise ratios for 1-butanol and 1-pentanol. The specific detector that allowed the array to detect the lowest concentration of a given odorant, defining the array detection threshold, thus varied somewhat depending on the affinity of the detectors for the odorant class of concern.

3.2. Comparison of detection thresholds for human and electronic noses

Data for human olfactory threshold values in detecting members of the homologous series of *n*-alkanes and 1-alcohols were obtained from the literature [30]. The values plotted in Fig. 1 represent mean detection thresholds as averaged over the work of many authors in testing many humans [30]. The averaging over many studies was performed in an attempt to obtain a mean detection threshold value without bias towards, or away from, the methodology of any particular investigator or with respect to any particular subgroup of humans that had been exposed to the odorants of interest during the course of a single study. The human detection threshold is defined as the lowest concentration of an odorant that an average human is able to detect relative to background air, without necessarily classifying the odorant type. This measure of odor detection sensitivity is consistent with the definition employed for the electronic nose. In fact, it can be postulated that in the case of humans, odorant detection at threshold likely involves the brain receiving a signal from only the olfactory receptor or receptors most strongly responsive to a given odorant. This is also consistent with the electronic nose detection threshold, as defined above. Comparisons were only made for volatile organic vapors as opposed to aroma active odorant vapors.

The data of Fig. 1 indicate that for the odorants studied in this work, the electronic nose detection thresholds are typically lower than the mean human detection thresholds, with the sole exception being *n*-pentane, for which the mean human detection threshold is slightly lower detection threshold than the electronic nose. Typically, the electronic nose detection thresholds are lower than mean human detection thresholds by a factor of 2–10, but of course the variance between human subjects and between human trials is such that the best performing humans in certain trials might well outperform the particular electronic nose implementation utilized in this work under the test conditions and detector configurations employed herein. In terms of thermodynamic activities, the fraction of a given odorant's vapor pressure (i.e. the partial pressure of the odorant, P, relative to its vapor pressure, P^0) at which the detection threshold lies for the electronic nose is in the range of 2.0×10^{-5}–6.0×10^{-5} for the odorants studied herein. For comparison, for the same set of test odorants the minimum fraction of an odorant's vapor pressure that is detectable by the average human is in the range of 4.9×10^{-5}–9.0×10^{-4}.

The underlying physicochemical principles for the odor detection threshold trend have recently been elucidated for certain detector compositions of the polymer composite electronic nose [31,32], but the analogous principles are not fully defined for the human olfactory system. Carbon black/organic-polymer composite electronic nose detectors exhibit similar steady state relative differential resistance response levels when exposed to most odorants at a constant value of P/P^0, due to the thermodynamic relationships between the chemical potential of the analyte in the gas phase and the mole fraction of analyte that will sorb into the polymeric phase under equilibrium conditions [29]. Thus, the electronic nose would be expected to exhibit similar detection thresholds for the tested odorants in terms of the minimum detectable fraction of vapor pressure (i.e. $P/P^0 \sim 4.0 \times 10^{-5}$), and this behavior was in fact observed experimentally herein. Humans also exhibit a trend in mean detection threshold of these odorants that tracks with the vapor pressure of the odorant, presumably reflecting at least in part the tendency of the odorant to sorb into the mucous. For the compounds evaluated in this study, the mean human odor detection threshold value is somewhat higher than the detection threshold of the current conducting polymer composite electronic nose. Given the standard deviations of the detection thresholds over various trials and groups of humans, there is some error in the absolute comparison of these two types of data sets, but clearly the data indicate that the detection limits of the human and electronic nose systems are comparable for the odorants investigated in this work.

We note, however, two significant classes of exceptions, notably the cases of thiols and biogenic amines, for which human odor detection thresholds are several orders of magnitude lower than those of the electronic nose. This suggests the presence of either highly specific receptor types and/or highly specific processing algorithms in the human olfactory system towards these odorants. In addition, the human nose is highly sensitive to certain pyrazines, thiazoles, to some aldehydes, and to many other compounds that have aroma activity as opposed to merely being volatile organic compounds. Although we have not investigated the detection threshold behavior of the electronic nose to these compounds as part of the present study, we expect that the current implementation of the conducting polymer composite electronic nose will exhibit detection thresholds for these odorants that are significantly higher than the mean human olfactory detection thresholds for these classes of analytes.

3.3. Pairwise odorant discrimination abilities of the electronic nose versus pairwise odor discrimination abilities of humans and monkeys

3.3.1. Odorant discrimination ability of the electronic nose

Assessing the discrimination ability of the electronic nose requires a choice of a data analysis algorithm. We have

chosen to use a statistical approach, in which a hyperplanar decision boundary is drawn in the *n*-dimensional space that encompasses the steady state resistance response data from the array of *n*-detectors responding to the presence of an odorant. The electronic nose containing 10-detector types was able to discriminate pairwise between all tested odorants with a resolution factor of at least 3.7. The minimum value was observed for the case of *n*-hexanoic acid versus isohexanoic acid, while the median rf across all tested odorant pairs was 29. Assuming that the statistical distributions of the collected data samples are representative of the actual statistical distributions, an rf of ∼3.0 corresponds to a probability of ∼98% of correctly identifying an odorant as *a* or *b* as a result of a single presentation. Hence, the electronic nose can easily discriminate between all of the test odorant pairs evaluated in this study under the experimental conditions employed in our test protocol.

3.3.2. Comparison of the trends in discrimination abilities between the conducting polymer composite electronic nose and mammalian olfaction

Data assessing the abilities of monkeys (*Saimiri sciureus*) and humans to discriminate pairwise between various ester, alcohol and carboxylic acid odorants were obtained from Laska et al. [33–35]. In those experiments, an average probability of correctly distinguishing between a given pair of odorants was determined by averaging across multiple trials and multiple test subjects. The odorants were presented at a perceived intensity-matched vapor concentration that was arrived at via 1:100 dilution of the pure odorants with diethyl phthalate.

Because the electronic nose exhibited >99% statistical probability of correctly distinguishing between members of every tested analyte pair in a single presentation of analyte to the detector array, depicting the discrimination performance of humans and/or primates versus the discrimination performance of the electronic nose on a common, linear axis would yield essentially no information concerning the trends in electronic nose performance as a function of chemical differences between pairs of odorants. Thus, the measure of distinguishing ability for the electronic nose was taken as the resolution factor, which scales with the separation of the clustered odorant responses relative to the widths of the clusters in detector space, and which is a statistically meaningful quantity based on the variation of the data for repeated exposures of the detector array to analyte pairs of interest. The resolution factor values can be converted into percentage of correct decision rates using conventional statistical properties of Gaussian distributions of data relative to the separation of the mean values of the data sets. The measure of distinguishing ability for the humans and monkeys was taken as the percentage of correct decisions in the task of distinguishing between members of an odorant pair. The experiments with human subjects utilized a forced-choice triangular test, so that the probability of a correct decision by random chance was 33%, whereas random chance for the monkey experiments would produce a 50% correct decision rate. Figs. 2–4 display the data for odorant discrimination of isopentyl acetate from a series of other esters (Fig. 2), *n*-pentanoic acid from a series of other carboxylic acids (Fig. 3), and *n*-pentanol from a series of other alcohols (Fig. 4).

Several correlations are apparent between trends in the discrimination properties of the electronic nose, the monkey olfactory system, and the human olfactory system. In most cases, as the odorants become more chemically dissimilar, the members of an odorant pair become easier to discriminate for the electronic nose, monkeys and humans. For example, in Fig. 2a, the task of discriminating between isopentyl acetate versus isopentyl propionate, isopentyl butanoate, isopentyl pentanoate, and finally isopentyl hexanoate, becomes progressively easier for all three olfactory systems. This makes sense because the odorant molecules in a pair are becoming progressively more dissimilar structurally. Similarly, in Fig. 3b, *n*-pentanoic acid is more difficult for each of the three olfactory systems to discriminate from isopentanoic acid than from either of isobutanoic acid or isohexanoic acid.

There are also subtle differences in the discrimination trends. For example, in discriminating *n*-pentanoic acid from each of *n*-propanoic acid, *n*-butanoic acid, *n*-hexanoic acid and *n*-heptanoic acid (Fig. 3a), the electronic nose has more difficulty in discriminating *n*-pentanoic acid from the longer chain acids relative to the shorter chain acids. Conversely, both mammals can more easily discriminate *n*-pentanoic acid from *n*-hexanoic acid than from *n*-butanoic acid. A similar observation can be made from Fig. 4, which indicates that monkeys more easily discriminate 1-pentanol from 1-heptanol and 1-octanol than from 1-propanol and ethanol, while the opposite is true for the electronic nose. Typically, the chemical difference between consecutive molecules in a homologous series decreases with the addition of each additional carbon atom. Thus, the relative difficulty of the electronic nose in discriminating between longer chain molecules versus shorter chain molecules, with molecules in each task differing by the same number of carbon atoms, is readily understandable. The opposite observation in specific instances for mammals could possibly indicate odorant receptor proteins having geometrically defined binding sites that more effectively differentiate between certain odorant geometries than do the polymeric detectors used in the current implementation of the electronic nose. Observations confirming the differential responses of an olfactory receptor neuron in vitro as a function of odorant chain length have recently been published [9].

It is also interesting to note that for the pairs of odorants evaluated in this work, the quantitative discrimination performance of the conducting polymer composite electronic nose is significantly higher than that of the monkey or human olfactory system (cf. Figs. 2–4). Interestingly, the data of Buck and co-workers, who determined Ca^{2+}(aq) production rates for a collection of olfactory receptors in response to a

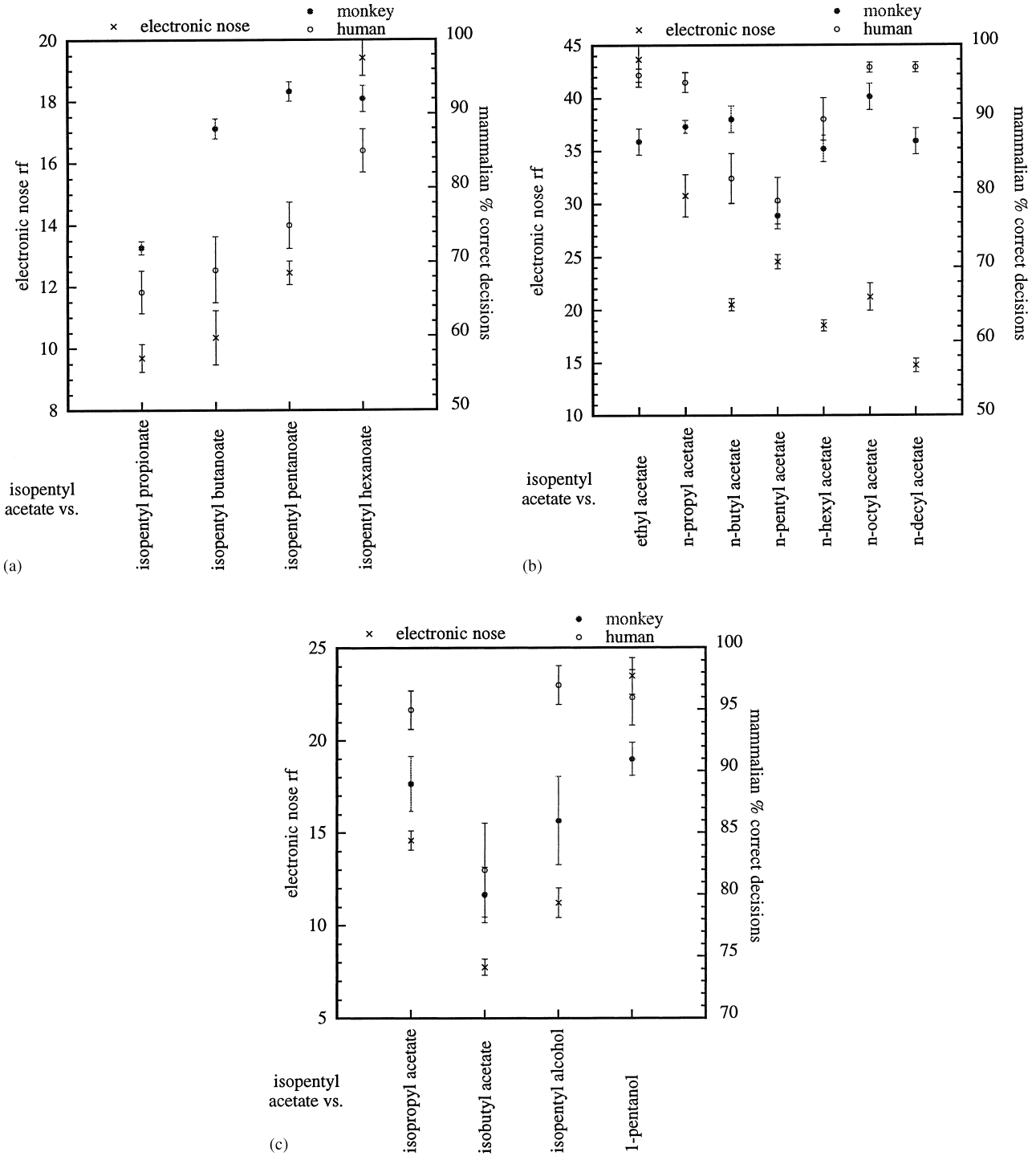
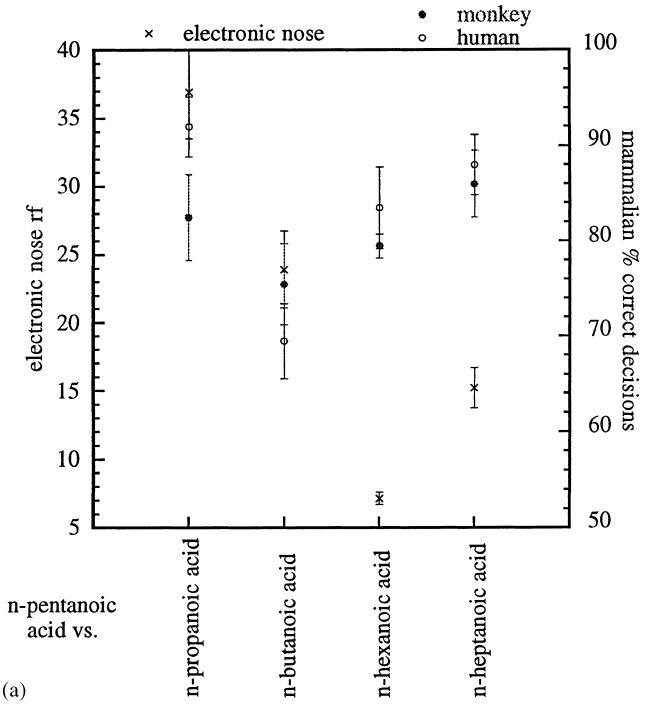
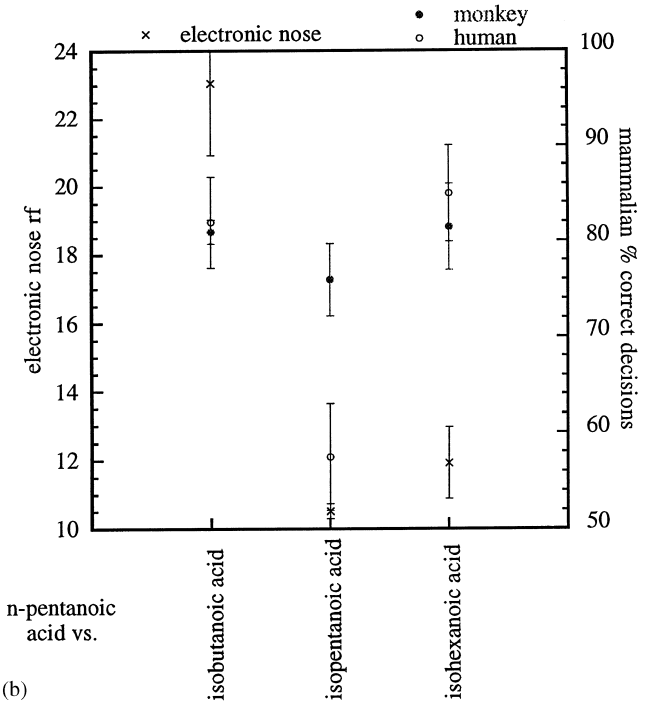


Fig. 2. Plots of trends in the abilities of the electronic nose, monkeys and humans to discriminate isopentyl acetate from other ester odorants (a,b) and to discriminate isopentyl acetate from isopentyl alcohol and 1-pentanol (c). The electronic nose data are plotted with reference to the left scale and the data points represent a mean resolution factor (rf). The monkey and human data are plotted with reference to the ordinate scale on the right of the figure and represent the mean probability of correctly discriminating between each specific pair of odorants averaged over 20 humans and over 5 monkeys, as experimentally determined by Laska [35]. The error bars represent 1 standard deviation unit of confidence in the mean values.

series of alcohols and carboxylic acids, show distinctly different receptor cell Ca^{2+} response patterns even for closely structurally-related compounds such as 1-octanol and 1-nonanol [9]. Reference to Fig. 4 indicates that humans and monkeys cannot effectively discriminate 1-pentanol and 1-hexanol nearly as well as their discrimination performance on more chemically dissimilar odorants. More chemically dissimilar receptor firing patterns might be expected for 1-pentanol relative to 1-hexanol than for 1-octanol relative to 1-nonanol because 1-pentanol is more chemically dissimilar



(a)



(b)

Fig. 3. Plots of trends in the abilities of the electronic nose, monkeys and humans to discriminate between *n*-pentanoic acid and two series of other carboxylic acid odorants. The electronic nose data are plotted with reference to the ordinate scale on the left of the figure, and the data points represent a mean resolution factor (rf). The monkey and human data are plotted with reference to the ordinate scale on the right of the figure and represent the mean probability of correctly discriminating between each specific pair of odorants averaged over 10 humans and over 4 monkeys, as experimentally determined by Laska [34]. The error bars represent 1 standard deviation unit of confidence in the mean values.

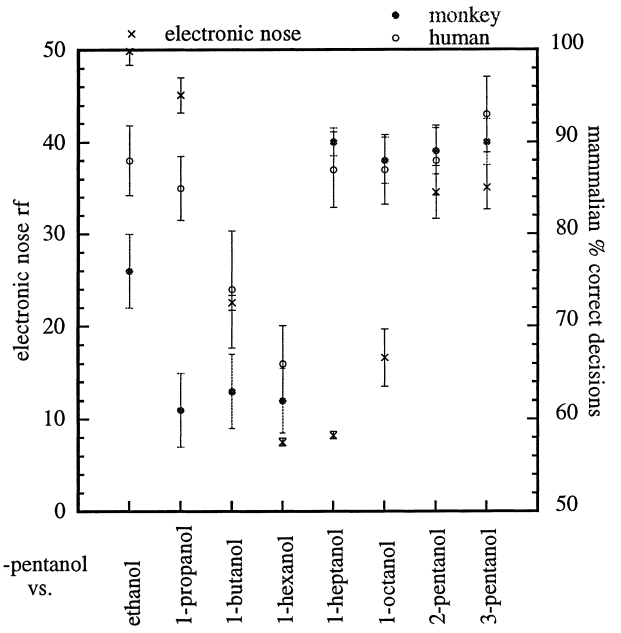


Fig. 4. Plots of trends in the abilities of the electronic nose, monkeys and humans to discriminate between 1-pentanol and a series of other alcohol odorants. The electronic nose data are plotted with reference to the ordinate scale on the left of the figure, and the data points represent a mean resolution factor (rf). The monkey and human data are plotted with reference to the ordinate scale on the right of the figure, and represent the mean probability of correctly discriminating between each specific pair of odorants averaged over 10 humans and over 4 monkeys, as experimentally determined by Laska et al. [33]. The error bars represent 1 standard deviation unit of confidence in the mean values.

to 1–hexanol than is 1-octanol relative to 1-nonanol. If this expectation is found to be valid experimentally, it would imply that the processing in the olfactory system of humans and monkeys results in a reduced ability to discriminate odors relative to the inherent differences in data content arising from the receptor response pattern produced by the outputs of the receptors in the olfactory bulb.

Several other factors could potentially confound the comparisons made above between the discrimination characteristics of the biological and electronic olfaction system for the compounds of interest in this work. First, the electronic nose measurements were collected for analytes in a background of laboratory air, while the human and primate discrimination data were collected for analytes diluted in diethyl phthlate. The human and primate data were also collected using higher background humidity levels than those in the air background used in the electronic nose discrimination measurements. The steady state relative differential resistance signals from carbon black-polymer composite detectors exposed to a wide series of test odorants have been shown to be essentially independent of whether the background ambient is pure air or is instead air with other analytes present [25]. Thus, introduction of diethyl phthlate as a background ambient component into the electronic nose measurements, and/or an increase in humid-

ity in the background carrier gas, would not be expected to produce a significant difference in the electronic nose discrimination performance relative to the data reported herein, and therefore, is not expected to significantly affect the comparisons in discrimination abilities discussed above. In addition, although the steady state response time for some of the electronic nose detectors was longer than the detection times used to evaluate the performance of the human system, the response time of the electronic nose detectors was not used as a classifying feature of the data, and only steady state values were utilized in the data analysis. The response times of the electronic nose detectors are a strong function of the system design, the delivery system characteristics, the polymer film thickness in the detectors, the detector readout electronics, and other properties which could be readily optimized if one wanted to reach steady state values for all detectors in a 1–5 s timescale. We have therefore used only the more fundamental, steady state response values of the electronic nose (which are ultimately not system configuration dependent) in our comparisons with the discrimination characteristics exhibited by the mammalian olfactory system.

An additional factor to be considered in comparing biologically-based olfaction to that exhibited by artificial devices is that the human olfactory system is non-linear in its response with respect to the concentration of analyte and/or analyte mixtures [36] whereas, the electronic nose signals from an individual detector are a linear function of the concentration of analyte in the gas phase, at least for partial pressures of odorants up to 5% of an analyte's vapor pressure at room temperature [25]. The discrimination metric for the electronic nose between an analyte pair is thus not a strong function of the analyte concentration (except as the variance between the classes of data is increased when the noise floor is closely approached). This behavior is not true for the biological system, however, in that discriminability can be a strong function of odorant concentration. Thus, for odorants whose perceived olfactory odor quality changes as the odor intensity changes, precise comparisons between discriminability of odorant pairs of the human and electronic nose will be dependent on the precise conditions under which the comparisons are made. In this work, we have chosen to make the comparison for odors from literature data that have been collected at a commonly perceived odorant intensity level for humans and monkeys, and for which electronic nose data have been obtained at a common thermodynamic activity level for each analyte. Furthermore, the activities of analyte in the gas phase were comparable between the human and primate studies and those used in the electronic nose performance evaluation. Information on the dependence of the mammalian olfactory discriminability of odorant pairs as a function of odorant concentration will be very valuable in making more robust comparisons between biological and artificial systems and ultimately in constructing an artificial device that mimics functionally certain aspects of human olfaction.

4. Conclusions

The results presented herein show some interesting similarities between the system-level performance features of the electronic nose and those of mammalian olfaction. Specifically, for the volatile organic, non-aroma active odorants evaluated in this work, the absolute detection thresholds and trends in the detection thresholds of the conducting polymer composite electronic nose are similar to trends in mean detection thresholds of humans. The electronic nose can typically detect a minimum odorant partial pressure of approximately 4×10^{-5} of the odorant's vapor pressure, which is comparable to the mean human detection thresholds reported for the particular odorants evaluated in this study. Aroma active compounds would be detectable at lower concentration levels by the human olfactory system than by the existing electronic nose implementation. Some similarities were also found to exist in odorant discrimination abilities between the systems, in that odorants typically become easier to discriminate pairwise for primates, humans, and the electronic nose as the members of an odorant pair become more chemically dissimilar structurally. The quantitative, statistically based discrimination performance of the conducting polymer composite electronic nose was significantly higher than that of the monkey or human olfactory system for the particular pairs of odorants that were evaluated in this study. The quantitative comparisons between the electronic nose and mammalian olfaction provided in this study are an initial contribution towards the ambitious goal of designing an electronic analogue to the mammalian olfactory sense.

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