

Limits of Recognition for Binary and Ternary Vapor Mixtures Determined with Multitransducer Arrays

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The discrimination of simple vapor mixtures from their components with polymer-coated multitransducer (MT) arrays as a function of the absolute and relative concentrations of those components is explored. The data set consists of calibrated responses to 11 organic vapors from arrays of 5 or 8 microsensors culled from a group of 5 cantilever, 5 capacitor, and 5 calorimeter transducers coated with 1 of 5 different sorptive-polymer films. Monte Carlo methods are applied to simulate error-enhanced composite responses to all possible binary and ternary mixtures of the 11 vapors, and principal component regression models are established for estimating expected rates of recognition as a function of mixture composition. The limit of recognition (LOR), defined as the maximum recognizable mixture composition range, is used as the metric of performance. With the optimal 8-sensor MT array, 19 binary and 3 ternary mixtures could be identified (i.e., discriminated from their components) with <5% error. The binary-mixture LORs are shown to decrease with increases in the baseline noise levels and random sensitivity variations of the sensors, as well as the similarity of the vapors. Importantly, most of the binary LOR contours are significantly asymmetric with respect to composition, and none of the mixtures could be recognized with <5% error at component relative concentration ratios exceeding 20:1. Discrimination of ternary mixtures from their components and binary subcomponent mixtures is possible only if the relative concentration ratio between any two of the components is <5:1. In comparing binary LORs for the best five-sensor single-transducer (ST) array to those of the best five-sensor MT array, the latter were larger in nearly all cases. The implications of these results are considered in the context of using such arrays as detectors in microanalytical systems with upstream chromatographic modules.

In the vast majority of studies on the application of microfabricated sensor arrays for the analyses of volatile organic compounds (VOC), the sensors employed in the arrays operate on

the same transduction principle.^{1–5} With most of these single-transducer (ST) arrays, a thin interfacial film of a sorptive polymer serves to reversibly concentrate vapors near the surface of each sensor. Although the differential sorption that occurs among sensors coated with different polymer films gives rise to array response patterns that can be used to differentiate one vapor from another, it is not generally possible to determine the components of mixtures of more than two VOCs using an ST array.^{6–12} This is because of the inherent limitations on both the range of vapor–polymer interactions and the features of those interactions probed by the underlying transducer.^{6,13}

The use of arrays of transducers operating on different principles, which we refer to as multitransducer (MT) arrays, should enhance the capability for vapor recognition by probing different aspects of the vapor–polymer interactions.^{13–17} In the context of VOC-mixture analyses, MT arrays are expected to afford better discrimination of mixtures from their components when compared to ST arrays and to extend the range of component-

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vapor concentrations over which such mixtures could be effectively analyzed.

In a recent study, we used a database of experimental responses to 11 individual vapors in Monte Carlo simulations to compare the expected performance of polymer-coated ST arrays and MT arrays for multivapor analysis.¹⁷ Sensors consisted of polymer-coated capacitors, cantilevers, and calorimeters. Assuming additivity in constructing the simulated composite responses to binary, ternary, and quaternary mixtures, optimally composed MT arrays outperformed optimally composed ST arrays having the same number of sensors in all cases. For problems involving the discrimination of individual vapors from other individual vapors in the calibration library, the difference in performance was not particularly large, owing to the relative simplicity of the problems. However, for binary and ternary mixture analyses there was a more significant advantage observed for the better MT arrays. With the use of an 8-sensor MT array that was determined to provide the best overall performance among all possible combinations of the 15 sensors under consideration, the 11 individual vapors could be differentiated from one another with an average error of only 1.2%, and 19 of the 55 possible binary mixtures that could be constructed from those 11 vapors could be discriminated from their component vapors with <5% error. Only 3 of the 165 possible ternary mixtures and none of the 330 possible quaternary mixtures could be accurately determined with this MT array.

The results of that study were obtained under the constraints that all of the components of the mixtures were present at the same signal-to-noise ratio and that the concentrations of the vapors were all greater than 5 times their respective limits of detection (LOD). Since the response patterns used to discriminate vapor mixtures from their components will generally degrade at low concentrations due to increased noise in the sensor signals, it is important to consider the range of absolute concentrations over which reliable recognition is possible. In addition, since recognition will also degrade as the relative concentration of the minority component(s) decrease, it is important to consider performance over a wide range of relative concentrations.

The "limit of recognition" (LOR) was first introduced in 1998 as an additional metric by which microsensor arrays could be assessed.¹⁸ For individual-vapor recognition problems, the LOR is defined as the lowest concentration at which a vapor can be reliably recognized among a predefined set of interfering vapors on the basis of its sensor array response pattern. It complements the LOD as a performance assessment parameter for microsensor arrays. Extension of the LOR concept to vapor mixture analyses was reported subsequently, and the methods for defining and assessing mixture LORs were illustrated using a 16-vapor data set obtained with an ST array of 6 polymer-coated surface acoustic wave (SAW) sensors.⁶

Briefly, since mixture recognition varies as a function of both the absolute and relative concentrations of the components, the mixture LOR is defined as an m -dimensional region, where m is the number of components in the mixture, whose boundary corresponds to the threshold between recognizable and unrecognizable mixtures based on some predetermined level of acceptable recognition error (e.g., 5%). For a binary mixture, the LOR

is defined as the area of a planar region; for a ternary mixture, it is defined as the volume of a polyhedron and so on. The size of the region reflects the range of component concentrations over which a mixture can be analyzed. As the concentration ratio of the mixture components becomes larger, it becomes more difficult to differentiate patterns of the mixture from patterns of the component vapors (binary and higher) and their lower-order mixtures (ternary and higher). Comprehensive analysis generally demands that the LORs be evaluated probabilistically, and by convention, a default threshold recognition rate (RR) of 95% is used.^{6,18} The corresponding LOR is designated as the LOR₉₅.

In this article, we extend our recent study of MT-array performance to address the influence of changes in absolute and relative vapor concentrations on the ability of an MT array to recognize binary and ternary mixtures by use of the LOR. With the use of the optimal 8-sensor MT array identified in the original study, the LORs for binary mixtures are evaluated and discussed. The effects of baseline sensor noise and random sensitivity fluctuations on the LOR are examined for representative binary mixtures. The asymmetry of the LOR profiles with respect to the component-vapor concentrations is then characterized and rationalized. Ternary-mixture LORs determined with this MT array are then addressed briefly followed by a comparison between an optimal 5-sensor MT array and the best of the 5-sensor ST arrays in the data set with regard to their resilience to concentration variations in binary mixtures. The practical implications of the results for vapor mixture analyses by microanalytical systems that might incorporate MT arrays as detectors downstream from a chromatographic separation module are discussed.

EXPERIMENTAL SECTION

Data Set Description. The primary data set consists of calibrated responses to the vapors of 11 VOCs from 15 sensors: 5 capacitors (CAP), 5 cantilevers (CAN), and 5 calorimeters (CAL). One of each type of transducer was coated with one of the following polymers: ethyl cellulose (EC), poly(cyanopropylmethylsiloxane) (PCPMS, 10% cyano groups), poly(dimethylsiloxane) (PDMS), poly(epichlorohydrin) (PECH), and poly(etherurethane) (PEUT). Sensor responses were collected for the following 11 VOCs over a range of concentrations: *n*-heptane (HEP), *n*-octane (OCT), toluene (TOL), methanol (MOH), ethanol (EOH), 1-propanol (POH), ethyl acetate (EAC), chloroform (CHL), carbon tetrachloride (CCL), trichloroethylene (TCE), and perchloroethylene (PCE). All of the calibration curves were linear and the sensitivity of each vapor-sensor pair determined from the slope was used as the starting point for all simulations. Details about the transducers, polymer structures, film deposition, vapor generation, and sensor calibrations can be found in refs 13 and 17.

Monte Carlo Simulations and EDPCR Models. To assess the expected performance of different sensor arrays for different vapor mixtures, Monte Carlo simulations were coupled with extended disjoint principal components regression (EDPCR) classification models. In this approach, measurement error is superimposed on calibrated response values as a way of simulating the variations in sensor output signals expected during actual operation. Error-enhanced response patterns for individual vapors and their mixtures from each array under consideration are then compared to stored library patterns using EDPCR to determine if the vapor or vapor mixture has been correctly recognized. For

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each mixture, 500 simulated response patterns were generated, from which statistical estimates of the RR (%) were derived. Further details of this approach to sensor–array evaluation can be found elsewhere.^{6,8,17,19}

Two sources of error were included in the Monte Carlo error model employed in this study: random sensitivity variations and baseline noise. The former was estimated for each of the 165 vapor–sensor combinations from the relative standard deviation (RSD) of the slope of each calibration curve.¹⁷ Values ranged from 4–13%, and for the simulations performed here the average of 7% was used in all cases. The average root-mean-square (rms) baseline noise values were determined experimentally as 2 Hz, 1 Hz, and 5.5 mV for the coated CAP, CAN, and CAL transducers, respectively.

For all simulations, vapor concentrations were expressed as multiples of the LOD (see ref 17 for tabulations of the LOD values). The LOD is defined for the array as a whole, meaning that it is determined by the highest LOD value among the individual sensors in that array. Specifying the absolute and relative concentrations as multiples or fractions of the vapor LODs facilitates comparisons across all vapor mixtures among arrays constructed from transducers with different units of measure. For this data set, LODs for a given vapor among the transducers of a given type coated with different polymers varied by ≤ 17 -fold, while those for a given vapor among different transducers with the same polymer coating varied by as much as 2 orders of magnitude.

For a given binary mixture, each analysis entailed discriminating the response pattern of the mixture from those of the constituent vapors. The absolute concentrations of the components ranged from $0.1\text{--}1500 \times \text{LOD}$. The concentration of one component at a time was varied in seven discrete increments (0.1, 0.5, 1, 5, 10, 15, and $20 \times \text{LOD}$) while the concentration of the second component was stepped through discrete increments corresponding to relative concentration ratios (RCR) of 1:75 to 75:1 (again, expressed as multiples of the component-vapor LODs) with respect to the first component. For the ternary cases, each analysis entailed discriminating the response pattern of the mixture from those of the constituent vapors and their binary mixtures. The concentration of one component at a time was varied in 5 discrete increments (1, 5, 10, 15, 20, and $30 \times \text{LOD}$) while the concentrations of the second and third components were individually stepped through 20 discrete increments between ratios of 1:10 to 10:1 (in terms of the LOD of each vapor) with respect to the first component. For the purposes of these analyses, which extend beyond the concentrations spanned during calibration, it is assumed that sensor responses remain linear and that composite responses to mixtures remain equivalent to the sum of the responses to the component vapors.

The manner in which we have formulated the recognition problems in this study is relevant to the situation where the sensor array is used as the detector for a microsystem with an upstream separation column. Differential retention reduces the number of vapors simultaneously presented to the sensor array, and retention times can be used a priori to constrain the subset of possible vapors subject to consideration at any given point in the analysis.²⁰ This justifies limiting the mixture-analysis problem to one where

1–3 specific vapors might be present simultaneously within a retention-time window, perhaps as a set of unresolved or partially resolved peaks, and the identity (and quantity) of each of those that are actually present needs to be determined. Thus, instead of having to search through the entire library of vapor response patterns associated with a complex mixture, the identity of the unknown vapors is determined from a search of the subset of vapors whose peaks fall into the specified retention-time window. For a binary mixture, the problem is simply to distinguish the mixture from its two constituent vapors. For a ternary mixture, the problem is to distinguish the mixture from the three individual vapors as well as the three binary mixtures that could be composed from those vapors. In addition to simplifying the pattern recognition problem, the computational time is also significantly reduced.

MT and ST Arrays. From our previous analyses of these data, the best overall performance, in terms of the recognition rates for all possible individual vapors and mixtures, was provided by an 8-sensor MT array of the following sensors: CAP-PCPMS, CAP-PDMS, CAN-EC, CAN-PEUT, CAL-EC, CAL-PDMS, CAL-PECH, and CAL-PEUT.¹⁷ This array was considered to be “universal” and is therefore abbreviated as the MT-U array. Out of the 55 possible binary mixtures one can create from 11 vapors, 19 could be recognized by the MT-U array with an $\text{RR} \geq 95\%$ (assessed over an absolute concentration range of $5\text{--}20\text{LOD}$ and an RCR of 1:1), and most of the analyses described below focus on these binary mixtures or subsets thereof. Out of 165 ternary mixtures that could be created from the 11 vapors, an $\text{RR} \geq 95\%$ could be achieved (and the LOR_{95} defined) for only 3 mixtures by the MT-U array for the same absolute and relative concentrations as mentioned above. Therefore, in order to increase the number of mixtures that could be considered, the threshold RR value was reduced to 90%, which yielded nine ternary mixtures with finite LOR_{90} values.

Among the 5-sensor ST arrays, the CAP array provided the best performance, with RR values $>95\%$ for 11 of the 55 binary mixtures ($5\text{--}20\text{LOD}$; $\text{RCR} = 1:1$). For the purpose of comparing the performance of ST and MT arrays, an optimal 5-sensor MT array, consisting of those sensors that yield the highest average recognition rate among all of the 55 binary mixtures, was selected. It consists of the following sensors: CAP-PCPMS, CAP-PDMS, CAN-PEUT, CAL-EC, and CAL-PEUT.¹⁷ This array was capable of achieving an $\text{RR} > 95\%$ for 12 binary mixtures, 11 of which were the same as those for which the CAP array provided finite LOR_{95} values.

Recognition Surfaces and LOR Contours. RR values calculated over all compositions of a given mixture were used to construct three-dimensional recognition surfaces from which the LOR could be derived. For each recognition-surface plot, the mixture recognition rate (vertical z -axis) is presented as a function of the absolute concentration of the minority component (y -axis) and the RCR (x -axis) (see Figure 1). Absolute concentrations are presented in multiples of the LOD of the minority mixture component, spanning a range of $0.1\text{--}20\text{LOD}$, with recognition assessed at seven absolute concentration values within this range. Beyond 20LOD , the LOR boundary does not change significantly so the plots are truncated at this value of absolute concentration. For the left-hand side of the plots (i.e., RCRs of 1:1–75:1), the absolute concentrations on the y -axis correspond to one of the

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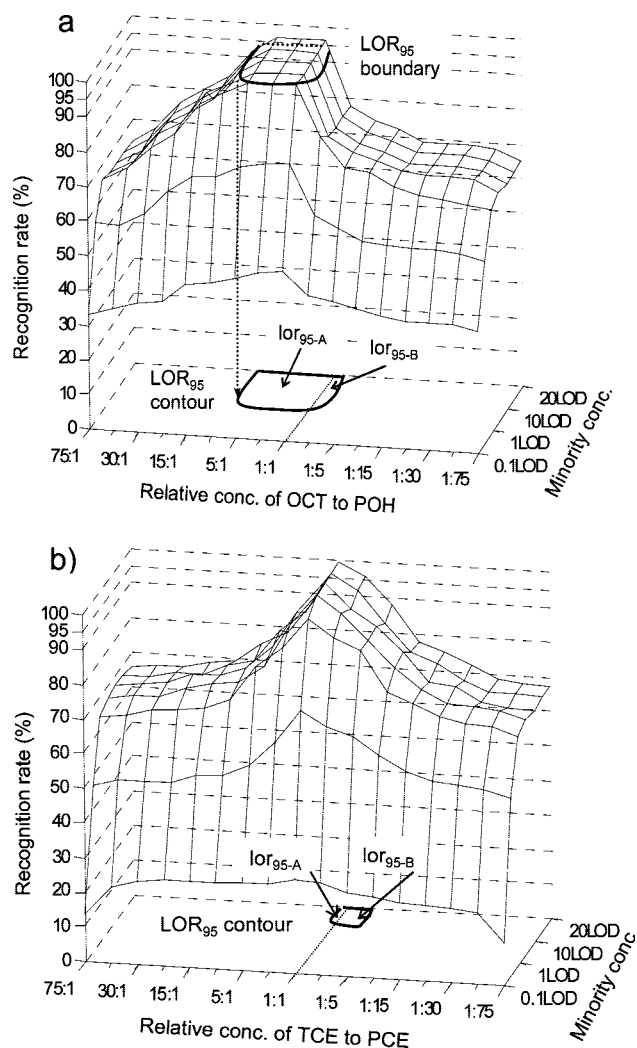


Figure 1. Recognition surfaces and projected LOR_{95} contours for two binary mixtures derived from simulated responses from the 8-sensor MT-U array: (a) *n*-octane + 1-propanol ($LOR_{95} = 120$) and (b) trichloroethylene + perchloroethylene ($LOR_{95} = 16$). mixture components and for the right-hand side (i.e., RCRs of 1:1–1:75) they correspond to the other component. The plots are labeled with the names of each vapor in a manner that assists with interpretation. Each surface consists of 119 coordinate points that define the RR for the absolute and relative concentrations of interest. By connecting the points corresponding to an RR of 95% on the *z*-axis, a boundary is defined corresponding to the LOR_{95} compositions for the mixture. The area of the contour projected on the *x*–*y* plane provides a convenient means of summarizing the LOR_{95} values of binary mixtures.

To quantify the area of the irregular LOR_{95} contour, the coordinates of the *x* and *y* axes are transformed in a manner that preserves the spatial relationships of the data but permits interpolation between the discrete points at which the RRs are evaluated.²¹ Since the units of the LOR_{95} become arbitrary, we have adopted the convention of expressing the LOR_{95} without units.

(21) The LOR_{95} is determined on the basis of RR values at rather widely spaced discrete coordinates along both the RCR and LOD axes, raising a question about the precision of the area calculation. However, a series of comparisons was made to show that the area calculated this way differed by only 3%, on average, from the area calculated on the basis of RR values at unit resolution on both axes.

Although the binary LOR_{95} can be used to rank different arrays in terms of their resilience to composition changes, the quantity itself is rather intangible. It is useful therefore to summarize further the LOR_{95} by selecting a single absolute concentration value and to calculate the magnitude of the limiting RCR along this cross section (*y*-axis coordinate), which gives the range of relative concentrations over which an $RR \geq 95\%$ can be achieved. Since the “depth” of the LOR_{95} has a maximum value of 20 (i.e., 1–20LOD), and the RR does not usually change radically in the range of 5–20LOD, the binary-mixture LOR_{95} values will generally vary more due to differences in this limiting RCR than due to differences in the absolute concentration range. Thus, this is a reasonable way of reducing the results to facilitate interpretation. We have chosen the 10LOD coordinate for this cross-sectional metric, because 10LOD is often used as the “limit of quantitation” in analytical measurements. Accordingly, the limiting RCR is designated as RCR_{10} .

Two approaches to quantifying the RCR_{10} could be used. In one, the length on either side of the 1:1 RCR point can be calculated separately. In the other, the total length can be calculated by merely dividing the RCR value on one side of the 1:1 RCR point by that on the other side (e.g., 5:1/1:2 = 10 for the case where the LOR has RCR_{10} boundaries at 5LOD:1LOD and 1LOD:2LOD). Although the latter approach is conceptually sound, from a practical standpoint it is problematic because, by definition, the minority component changes as the 1:1 RCR point is crossed and it takes on the value of 10LOD. However, to the extent that it portrays the “fold-range” over which a mixture can be recognized at $\geq 95\%$, this approach to evaluating the RCR_{10} serves its purpose. As it turns out, there is a strong linear correlation ($r^2 = 0.96$) between the values of RCR_{10} and LOR_{95} for the 19 mixtures analyzed by the MT-U array in this data set, which supports its use as done here.

For ternary mixtures, it is not possible to capture all of the variables affecting recognition in a single contour plot because four dimensions are required. In the approach taken here, two-dimensional sections are created at a fixed, discrete level (see above) of absolute concentration for the first component and over a range of RCRs for the second and third components. The average of the LOR_{95} contour areas over several discrete absolute concentration increments gives a score for the ternary mixture that varies in proportion to the total range of reliably analyzed concentrations. This way, a ternary mixture analysis is reduced to a series of binary mixture analyses and an average LOR score can be calculated accordingly to assess array performance.⁶

Monte Carlo simulations and EDPAC routines were performed in Excel using macros written in Visual Basic. Calculations of LOR contour areas, plots of the recognition surfaces, and other computations were performed using Matlab 7 (MathWorks, Inc., Natick, MA).

RESULTS AND DISCUSSION

LORs for Binary Mixtures. The LOR_{95} values determined with the MT-U array for all 19 binary mixtures are presented in Table 1. They span a 7.4-fold range, from 16 to 120. The corresponding RCR_{10} values, presented in Table 2, range from 5 to 20, indicating that the minimum relative concentration range over which a binary mixture can be analyzed is 5-fold and the

Table 1. LOR Evaluations of 19 Binary Mixtures Using Simulated Data from the 8-Sensor MT-U Array

components													
A ^b	B ^b	RR (%) ^a	LOR ₉₅	LOD _A ^b	LOD _B ^b	S _A ^c	S _B ^c	E _{AB} ^d	e _A /e _B ^e	A ^f	P _A ^g	P _B ^g	P _A /P _B
HEP	MOH	97.4	42	2100	6500	0.28	0.43	1.9	1.6	6.2	590	2800	0.21
HEP	EOH	99.8	36	2100	2400	0.28	0.78	1.9	1.8	4.0	590	1900	0.31
HEP	POH	99.2	24	2100	1160	0.28	2.1	1.8	2.1	7.1	590	2460	0.24
HEP	EAC	100	56	2100	1100	0.28	0.42	1.6	0.85	0.43	590	460	1.3
HEP	CHL	99.8	120	2100	1300	0.28	0.78	1.9	1.7	1.5	590	1000	0.56
HEP	TCE	100	40	2100	620	0.28	0.50	1.8	0.64	0.23	590	300	1.9
OCT	MOH	98.2	24	770	6500	0.81	0.43	1.6	2.5	9.1	630	2800	0.22
OCT	EOH	99.6	24	770	2400	0.81	0.78	1.7	2.5	3.3	630	1900	0.33
OCT	POH	99.2	120	770	1200	0.81	2.1	2.0	1.6	4.0	630	2460	0.26
OCT	EAC	100	38	770	1100	0.81	0.42	1.8	0.72	0.29	630	460	1.4
OCT	CHL	99.8	28	770	1300	0.81	0.78	1.9	1.1	1.2	630	1000	0.60
OCT	TCE	99.8	66	770	620	0.81	0.50	1.7	0.46	0.18	630	300	2.0
TOL	TCE	98.2	28	220	620	0.32	0.50	1.8	2.1	5.6	70	300	0.22
EAC	CCL	99.8	60	1100	1200	0.42	0.12	1.9	0.39	0.15	460	140	3.2
EAC	PCE	99.8	72	1100	230	0.42	0.58	1.9	0.27	0.10	460	140	3.4
CHL	CCL	98.4	96	1300	1200	0.78	0.12	1.9	0.14	0.047	1000	140	7.3
CHL	PCE	97.8	84	1300	230	0.78	0.58	1.8	0.12	0.045	1000	140	7.7
CCL	TCE	100	34	1200	620	0.12	0.50	1.7	4.0	2.1	140	310	0.46
TCE	PCE	99.4	16	600	230	0.50	0.58	1.6	0.48	0.25	310	140	2.3

^a Average recognition rate determined at an RCR = 1:1 over a concentration range of 5–10LOD for each component. ^b Units = ppm. ^c Array sensitivity in units of response/ppm. ^d E_{AB} is the Euclidean distance between normalized vectors for mixture components A and B. ^e e_A and e_B are the Euclidean distances between the vectors for components A and B and the vector for their 1:1 mixture, respectively. ^f A is an index of asymmetry defined as the ratio of lor_{95-A}/lor_{95-B} (see Figure 1a). ^g P is the product of the LOD and S for a given mixture component. ^h Acronyms are defined as follows: *n*-heptane (HEP), *n*-octane (OCT), toluene (TOL), methanol (MOH), ethanol (EOH), 1-propanol (POH), ethyl acetate (EAC), chloroform (CHL), carbon tetrachloride (CCL), trichloroethylene (TCE), and perchloroethylene (PCE).

Table 2. Range and Asymmetry of Relative Concentration Ranges Evaluated at a Minority-Component Concentration of 10LOD (RCR₁₀) over Which the Recognition Rate of the Mixture Is ≥95%^a

Mixture Components		RCR ₁₀	Range of RCR ₁₀																		
A	B		10:1	9:1	8:1	7:1	6:1	5:1	4:1	3:1	2:1	1:1	1:2	1:3	1:4	1:5	1:6	1:7	1:8	1:9	1:10
HEP	MOH	6				(2:1)							(1:3)								
HEP	EOH	5					(4:1)						(1:1)								
HEP	POH	5						(9:1)					(1:2)								
HEP	EAC	9							(6:1)					(1:2)							
HEP	CHL	20	(16:1)											(1:1)							
HEP	TCE	6								(3:1)								(1:2)			
OCT	MOH	5					(2:1)						(1:9)								
OCT	EOH	5					(2:1)						(1:3)								
OCT	POH	20	(7:1)											(1:3)							
OCT	EAC	8								(1:1)					(1:6)						
OCT	CHL	5					(3:1)						(1:2)								
OCT	TCE	12								(3:1)								(1:5)			
TOL	TCE	5					(2:1)						(1:3)								
EAC	CCL	12								(2:1)								(1:7)			
EAC	PCE	14								(9:1)								(1:2)			
CHL	CCL	18								(2:1)										(1:8)	
CHL	PCE	16								(4:1)										(1:1)	
CCL	TCE	5					(10:1)						(1:2)								
TCE	PCE	5								(3:1)								(1:2)			

^a The column of entries for RCR₁₀ is the fold-range of relative concentration ratios for each mixture for which RR ≥ 95%. Each line spans that RCR range and shows the degree of asymmetry relative to the RCR = 1:1 value when concentrations are expressed as multiples of the LOD for each component. Values in parentheses at the end of a line are the corresponding RCR values in units of ppm. Acronyms are defined as follows: *n*-heptane (HEP), *n*-octane (OCT), toluene (TOL), methanol (MOH), ethanol (EOH), 1-propanol (POH), ethyl acetate (EAC), chloroform (CHL), carbon tetrachloride (CCL), trichloroethylene (TCE), and perchloroethylene (PCE) and in the Experimental Section.

maximum is 20-fold. At larger RCR values, the mixture is confused for one of the two mixture components.

In those cases where the LODs differ between the two components, the RCR₁₀ expressed in terms of actual vapor concentrations (e.g., part-per-million, ppm) will differ proportionally. Among the 19 mixtures, the largest component–LOD ratio is 8:1 (for *n*-octane–methanol) and the next-largest ratio is 6:1 for chloroform–perchloroethylene. With evaluation of the LODs

for each of the components of the mixture, it is possible to define the RCR₁₀ part-per-million-wise. These RCR₁₀ ranges are also presented in Table 2. The mixture of heptane + chloroform, which has one of the largest values of RCR₁₀ in terms of signal-to-noise ratio (i.e., 20), also has one of the larger RCR₁₀ values in terms of part-per-million (i.e., 16). In contrast, the mixture of carbon tetrachloride + trichloroethylene, which has one of the smallest RCR₁₀ values when defined in terms of signal-to-noise ratio (i.e.,

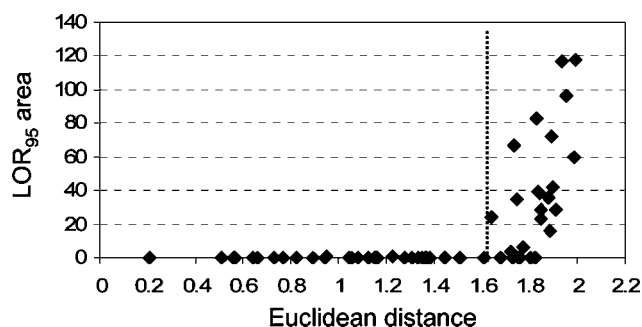


Figure 2. Relationship between the LOR_{95} and the Euclidean distance between the vectors of each mixture component for 55 binary mixtures. The vertical dotted line denotes the threshold Euclidean distance below which recognition is not possible.

5), has nearly the largest RCR_{10} value when defined by terms of ppm (i.e., 20).

Figure 1 shows two representative recognition-surface and LOR_{95} contour plots. In each case, the RR never exceeds that at an $RCR = 1:1$. This holds for all 19 binary mixtures and confirms the intuitive expectation that recognition becomes more difficult as the composition (or, more accurately, the array response vector) of the mixture becomes dominated by either component. This is consistent with findings from our previous study of binary LORs with polymer-coated SAW sensors.⁶

The rate of decline in RR on either side of the line corresponding to $RCR = 1:1$ is determined by the similarity in response patterns for the components, and the asymmetry in the decline in RR as a function of relative composition is related to the differences in the LODs and array sensitivities for each component. The surfaces do not change much as a function of absolute concentration above $\sim 5LOD$ (minority component). In contrast, as the concentration of the minority component falls below the LOD, there is a precipitous decline in RR commensurate with both the loss of sensors making a contribution to the response pattern and the increasing influence of baseline noise on the response patterns. All of these issues are addressed below.

Response Pattern Similarity. The correlation of the response-pattern similarity between the components of a binary mixture with the magnitude of the LOR_{95} was evaluated using the Euclidean distance, E_{AB} , as the similarity metric. Values of E_{AB} were determined on the basis of normalized response patterns, wherein each sensor response was divided by the sum of all sensor responses to an arbitrary concentration of the vapor. The magnitude of E_{AB} decreases with the similarity in the response patterns of the two vapors and for the 19 mixtures with finite LOR_{95} values, ranges from 1.6 to 2.0 (Table 1).

Figure 2 shows the correlation of the LOR_{95} with the component-vapor E_{AB} values. Data for all 55 binary mixtures in the original data set have been included to show that there is a threshold E_{AB} value of ~ 1.6 below which analysis is not possible (i.e., $LOR_{95} = 0$). Above this value, the LOR_{95} increases rapidly with E_{AB} in a roughly linear manner; however, the correlation is not strong enough to establish any sort of predictive model. Furthermore, even beyond the threshold E_{AB} , several mixtures cannot be analyzed. These anomalous cases are most likely attributable to the magnitude of the sensitivity error used in the Monte Carlo simulations and to the fact that neither the variability of responses

nor the relative or absolute vapor concentrations are accounted for in the E_{AB} calculation.

The recognition surface plots and LOR_{95} contours presented in Figure 1 are for the binary mixtures with the largest and smallest E_{AB} values among the 19 vapors with finite values of LOR_{95} : *n*-octane + 1-propanol and trichloroethylene + perchloroethylene, respectively. The large difference in LOR_{95} is apparent from a visual inspection of the surface plots. It is also apparent that above a minority-component concentration of 5LOD, the LOR_{95} is dictated by the RCR and not by the absolute concentration.

Sensitivity Variations and Baseline Noise. The ability to identify a vapor on the basis of its response pattern relies implicitly on the fidelity of that pattern over time which, in turn, relies on the reproducibility of the responses from the sensors in the array. Considered in the context of a microanalytical system, the reproducibility of sample volumes, flow rates, preconcentrator capture and desorption efficiencies, chromatographic retention, and temperature control must be considered. Fluctuations in any or all of the processes involved in signal generation can contribute to perturbations in response patterns that may undermine recognition via matching to library patterns.

The effect of sensitivity variations on the LOR_{95} was explored for several mixtures while the baseline noise levels of all sensors were maintained at their experimental values. Figure 3 shows the recognition surfaces and LOR_{95} contours for a representative binary mixture of *n*-heptane + ethyl acetate for sensitivity errors of 3, 5, and 10% applied randomly to the sensors in the MT-U array. This mixture gives a midrange LOR_{95} value and thus represents a recognition problem of moderate difficulty. The corresponding LOR_{95} values are 210, 88, and 0, respectively. The effect is quite significant, a 1.7-fold increase in sensitivity error (i.e., from 3 to 5%) leads to a proportional reduction in the LOR_{95} of 58% (i.e., $\sim 1/1.7$), and if the rms sensitivity variation is allowed to increase to 10%, then the mixture cannot be analyzed at any composition. These results serve to illustrate that stable (reproducible) sensor responses are essential for satisfactory recognition of mixtures over relevant concentration ranges.

To explore the effect of baseline noise on mixture recognition, analyses were confined to a concentration range of 0.1–5LOD where such noise has its greatest impact on response patterns.^{6,17} As noted above, below 1LOD at least one of the sensors will not be contributing a statistically significant response to the pattern produced by the array. Although high values of RR can be maintained for some mixtures, continued reductions in concentration inevitably lead to a decline in performance.¹⁸

The influence of baseline noise on the recognition surface and LOR_{95} is shown in Figure 4, again, for the binary mixture of *n*-heptane + ethyl acetate. As the noise level increases there is a commensurate reduction in RR and LOR_{95} values. The rate of reduction in RR is greater at lower concentrations (i.e., $< 1LOD$), but with increasing noise levels significant reductions are also observed in the 1–5LOD range. Note that the LOR_{95} contour shrinks along both the absolute and relative concentration axes; and for the example shown in Figure 4, a 10-fold increase in noise leads to ~ 4 -fold decrease in LOR_{95} (i.e., from 56 to 13). The general trend holds for other mixtures as well, although the dependence on noise levels is more acute for mixtures whose LOR_{95} values are initially smaller (i.e., for mixtures

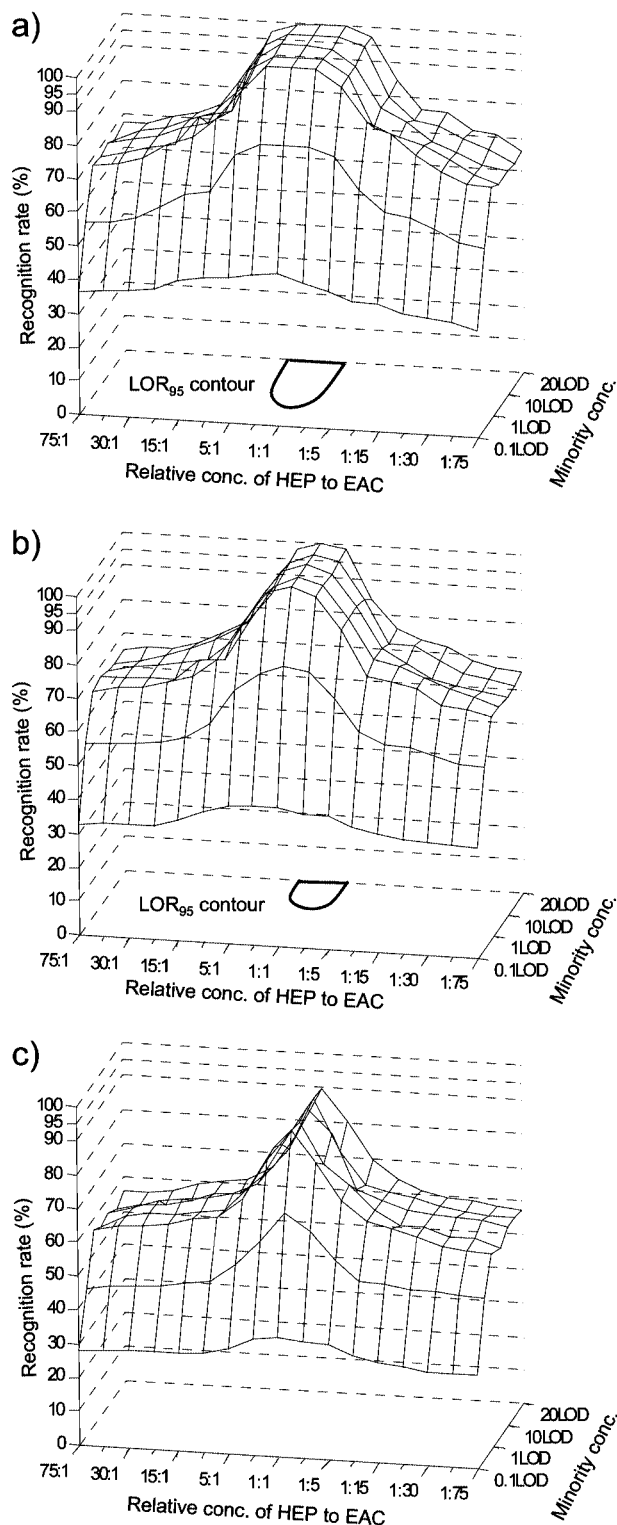


Figure 3. Recognition surfaces and LOR_{95} contours for the binary mixture of *n*-heptane and ethyl acetate as a function of assumed sensitivity error: (a) 3% ($LOR_{95} = 210$), (b) 5% ($LOR_{95} = 88$), and (c) 10% ($LOR_{95} = 0$).

whose components are more difficult to discriminate). In none of the cases considered did the noise level affect RR values above an absolute concentration of 5LOD, leading to the practical recommendation that sensors be operated above this concentration to avoid any possible influence of baseline noise on pattern fidelity.

Compositional Asymmetry in the LOR Contours. In nearly all cases, the LOR_{95} contours are significantly asymmetric with respect to composition. This is shown in Table 2 and it is what gives rise to the marked skew of the surfaces and contours with respect to the RCR of 1:1 in the example shown in Figure 1a. Taking the ratio of the LOR_{95} areas on each side of the 1:1 composition line, lor_{95-A} and lor_{95-B} , respectively, provides a way of quantifying the asymmetry (see Figure 1a and Table 1). We refer to this ratio as A in Table 1 and employ it here as the index of asymmetry. In only two cases does the value of A fall within the interval of 0.5–2. The greatest degree of asymmetry occurs for the mixture of chloroform + perchloroethylene with $A = 0.045$ (i.e., $1/22$).

The primary factor contributing to the asymmetry in the recognition contours is the difference in the sensitivity of the array, S , to each component. However, since we define concentration in terms of the LOD, differences in the component LODs will also contribute. Indeed, the ratio of the LOD- S product, P , of each component in the mixture is strongly correlated with the degree of asymmetry, and regressing A onto $(P_A/P_B)^{-1}$ for the 19 mixtures yields a line with an $r^2 = 0.986$. In physical terms, the product of LOD and S corresponds to the increase in the length of the array response vector per unit increase in concentration, where concentration is measured in multiples of the LOD (i.e., “ $\times LOD$ ”).

Note that the array sensitivity to each vapor corresponds to the Euclidean vector norm for that vapor as determined from the net contributions of all of the sensors. Mathematically, it is the square root of the sum of squares of each sensor's sensitivity to that vapor. The LOD, however, is determined by the single sensor in the array exhibiting the largest minimum response for the vapor. Thus, a vapor may have a high LOD but at the same time may have a high S value, since the two are not necessarily correlated.

The P values for the components of each mixture along with their ratio are compiled in Table 1. The recognition surface is always higher toward the component with the lower value of P . For the example shown in Figure 1a, $P = 630$ for *n*-octane and $P = 2\,500$ for 1-propanol; giving a ratio of about 1:4. Accordingly, $A = 4$ and the RR remains higher for mixtures rich in *n*-octane. For the mixture of *n*-heptane and ethyl acetate shown in Figure 3a, P_A/P_B is only 1.3:1 and the surface and LOR_{95} are correspondingly more symmetric ($A = 0.43$), with a slight preference for mixtures rich in ethyl acetate.

The need to account for the LOD in assessing asymmetry is an artifact of expressing concentration in these analyses as multiples of the LOD for each vapor. If concentrations were expressed in units of mass/volume or part-per-million, then the sensitivity ratio alone would determine the asymmetry. This is evident in Table 1 for the mixture of chloroform and carbon tetrachloride, where the LODs differ by <10% but $P_A/P_B > 7$ and $A = 0.053$. It is also evident in several entries in Table 2, where the direction of asymmetry actually reverses when the RCR_{10} values are evaluated in terms of part-per-million rather than “ $\times LOD$ ”.

The Euclidean distance between the mixture components can also be partitioned into the segments corresponding to the distances between each component and the mixture with an RCR

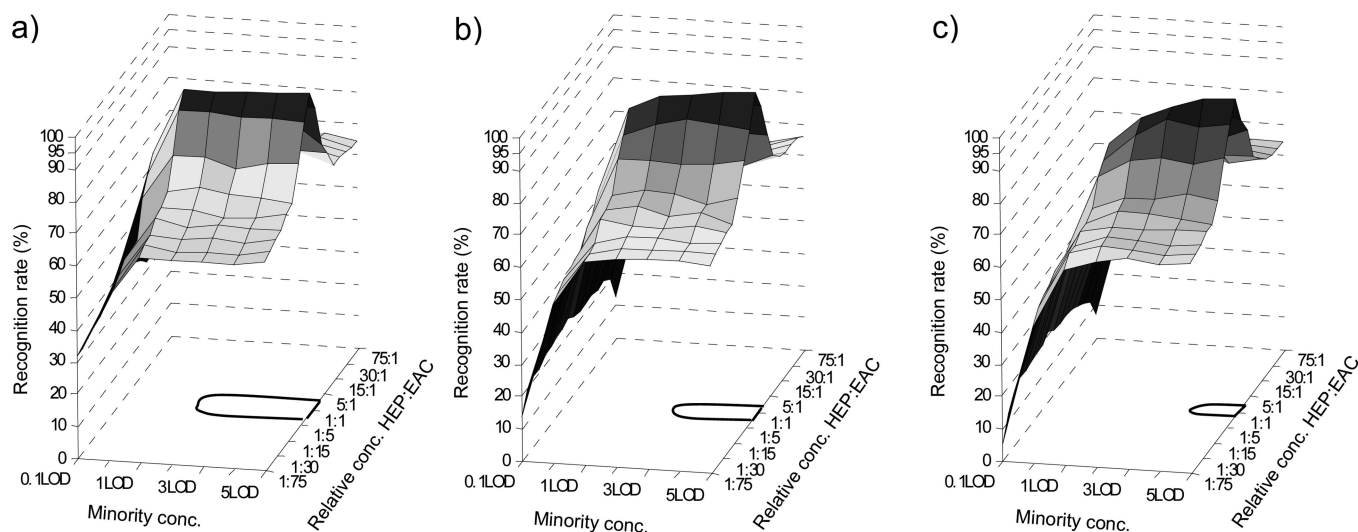


Figure 4. Effect of baseline noise levels on the LOR_{95} for the binary mixture of *n*-heptane + ethyl acetate: (a) average experimental rms noise ($LOR_{95} = 56$), (b) $5 \times$ rms noise ($LOR_{95} = 40$), and (c) $10 \times$ rms noise ($LOR_{95} = 13$). The concentration range shown spans from 0.1–5LOD, but LOR_{95} is calculated from 1–5LOD.

= 1:1. Here again, account must be taken of the differences in LOD values and array sensitivities of the mixture components. If the mixture components are present at equivalent signal-to-noise ratios then the composite response vector falls at the midpoint between the two individual component vectors in hyperspace. If the contribution of each component to the composite response is multiplied by its P value, then the resulting composite vector is shifted in the direction of the vapor with the larger value of P . After application of this weighting factor to each normalized response vector, the partitioned Euclidean distances between each individual-vapor vector and the 1:1 mixture can be determined. These are denoted here as e_A and e_B . By definition, the e_A/e_B ratio is directly proportional to P_A/P_B and therefore it should also be inversely related to the asymmetry index, A .

Accordingly, only small increases in the relative concentration of the vapor with the larger value of P in the mixture can be tolerated before the composite response pattern for the mixture can no longer be differentiated from that of the individual component. This is illustrated by the sharp decline in RR shown in Figures 1a and 3a as the composition of the mixture shifts from 1:1 toward compositions rich in this component. The fact that shifts in the other direction, toward compositions rich in the other component, permit higher RR values to be achieved over a wider RCR range is consistent with the greater Euclidean distance between the vector corresponding to the individual component and that for the 1:1 mixture.

The practical implications of the asymmetry are essentially superimposed on the overall constraint imposed by the LOR_{95} . As stated above, the maximum ratio of concentrations of mixture components that can be tolerated is about 20:1. Beyond this range, the minority component will not be recognized. Because of asymmetry, however, this range is not equally applicable to each component, and when the component to which the array is more sensitive becomes the majority component, the RCR over which recognition is possible is much smaller than when it is the minority component. In a microanalytical system where a chromatographic band is delivered to the array, these results have direct implications for assessing peak purity; if a minority component to which

the array is less sensitive is embedded within the peak corresponding to the majority component, it will not likely be detected.

LORs for Ternary Mixtures. Figure 5 shows cross-sectional LOR contours for the mixture of *n*-heptane + ethyl acetate + chloroform, which is one of the three ternary mixtures for which average RR values $\geq 95\%$ were obtained (5–20LOD at an RCR = 1:1:1). The panels show the iso-recognition contours at concentrations of 5LOD and 20LOD for each of the components. The coordinate axes are the RCRs for the other two components relative to the one whose concentration is specified (i.e., the minority component). In contrast to the general trend observed for binary mixtures, the recognition rate for the ternary mixtures continues to increase in the range of 5–20LOD but does not increase significantly at higher minority-component concentrations. Interestingly, at the 90% contour, the concentration dependence is reduced. None of the mixtures could be recognized at a minority-component concentration <5LOD, meaning that the LOR places a greater constraint on the analysis than does the LOD.

The LOR_{95} score (evaluated from 1–20LOD) for the mixture shown in Figure 5 is 4.0 and those for the other two ternary mixtures are both 3.5, reflecting the small range of concentrations over which they can be recognized. According to Figure 5, the largest RCR within the 95% contours is ~ 8 (i.e., from 4:1 to 1:2) regardless of which vapor is held constant, and the largest ratio of concentrations that can be recognized, in units of part-per-million, is $\sim 5:1$. The largest RCR values for the other two mixtures are comparable to these values.

The asymmetric distribution of the iso-recognition contours with respect to an RCR = 1:1 for the two components whose concentrations are allowed to vary in these cross sections is correlated with P_A/P_B , as observed with the binary mixtures. For the example shown, the values of P for *n*-heptane, chloroform, and ethyl acetate are, respectively, 590, 1000, and 460, which results in $P_A/P_B = 0.56$ for *n*-heptane–chloroform, 0.77 for ethyl acetate–*n*-heptane, and 0.46 for ethyl acetate–chloroform (see Table 1). Accordingly, the LOR_{95} contours in Figure 5 are skewed with respect to the RCR = 1:1 point toward ethyl acetate to the greatest extent, followed by *n*-heptane. That

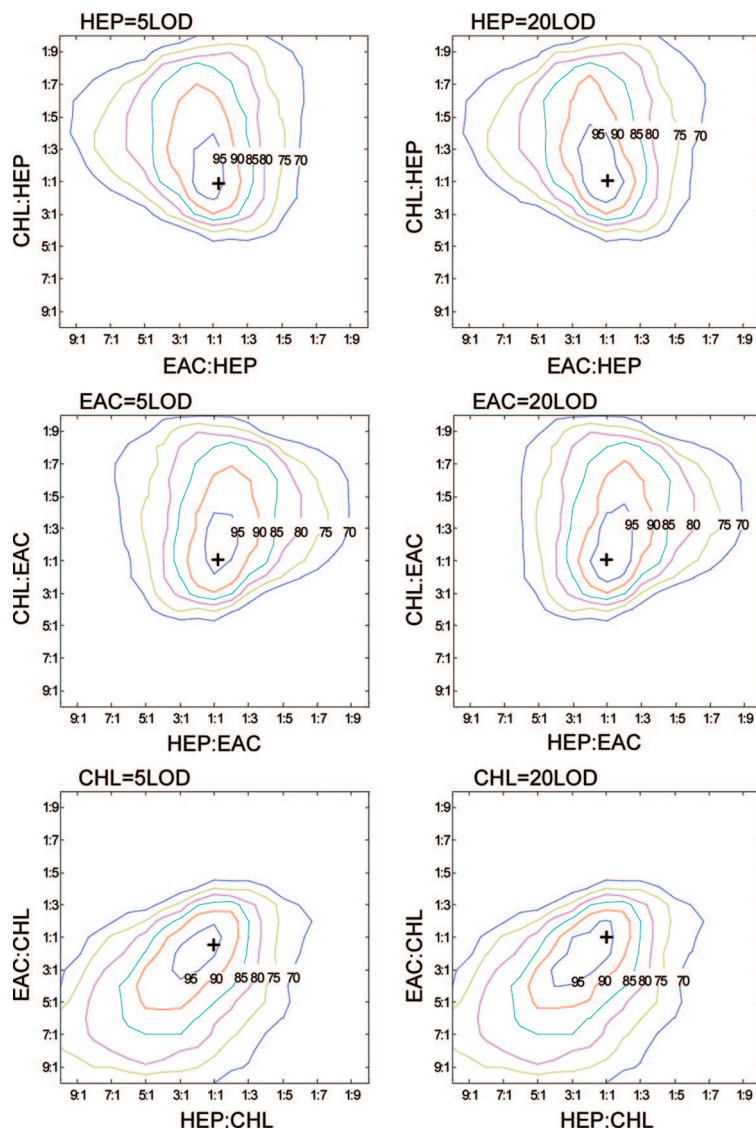


Figure 5. Cross-sectional LOR contours for the ternary mixture of *n*-heptane + chloroform + ethyl acetate at 5LOD and 20LOD for each of the three components. The *x*- and *y*-axes are the relative concentration ratios (in multiples of the LOD) of the indicated (varying) mixture component to the fixed component.

Table 3. LOR Evaluations of the Nine Ternary Mixtures Recognized at an RR Threshold of 90%

mixture components				cross-sectional LOR ₉₀ at six concentrations of component A ^b						LOR ₉₀ score ^c
A	B	C	RR (%) ^a	0.1	0.5	1	5	10	20	
OCT	POH	EAC	91.0	0	0	1.2	5.5	6.1	6.0	4.7
HEP	EOH	TCE	91.2	0	0	4.8	5.0	6.0	6.1	5.5
HEP	POH	EAC	92.0	0	0	2.5	4.4	5.4	5.2	4.4
OCT	EOH	TCE	92.0	0	0	5.0	5.3	7.4	7.2	6.2
OCT	MOH	EAC	92.8	0	1.3	12	15	16	16	15
HEP	MOH	EAC	93.4	0	1.5	14	14	16	15	15
HEP	EAC	CHL	95.2	0	4.5	10	13	13	13	12
HEP	EOH	EAC	95.4	0	4.7	13	16	17	16	16
OCT	EOH	EAC	96.2	0	11	14	18	19	20	18

^a Average recognition rate determined at an RCR = 1:1:1 over a concentration range of 5–10 LOD for each component. ^b Concentration is defined in multiples of the LOD. ^c The score is the average cross-sectional LOR₉₀ contour area determined from 1–20 LOD. Acronyms are defined as follows: *n*-heptane (HEP), *n*-octane (OCT), toluene (TOL), methanol (MOH), ethanol (EOH), 1-propanol (POH), ethyl acetate (EAC), chloroform (CHL), carbon tetrachloride (CCL), trichloroethylene (TCE), and perchloroethylene (PCE).

is, higher RR values are possible over wider concentration ranges when these two vapors are majority components. Similar

correlations are found for the other two ternary mixtures with finite LOR₉₅ values.

If the threshold RR is reduced to 90%, nine ternary mixtures give finite LOR_{90} values and trends can be explored. Table 3 presents the LOR_{90} scores for these mixtures as a function of the absolute concentration of the first component listed for each mixture. It is worth noting that the three mixtures with finite LOR_{95} values can be recognized at concentrations $< 0.5LOD$ using the 90% recognition criterion (i.e., LOR_{90}), while the other ternary mixtures cannot. Regardless, the cross-sectional LOR_{90} values do not increase significantly beyond a minority-component concentration of about $5LOD$. The LOR_{90} scores (from 1– $20LOD$) range from 4.7 to 18 and show a strong correlation with the average RR value determined at an RCR of 1:1:1 over the range of 5– $20LOD$.

Binary LORs for 5-Sensor ST and MT Arrays. The performance of the 5-sensor CAP ST array and the optimal 5-sensor MT array was assessed in the same manner as the MT-U array. Detailed results are tabulated in the Supporting Information accompanying this article (Tables SI-1 through SI-4). Key points are summarized here as they relate to the relative advantages of using MT vs ST arrays for multivapor determinations.

The fact that only 12 binary mixtures could be analyzed with an average $RR \geq 95\%$ (5– $10LOD$ at an RCR of 1:1) with this 5-sensor MT array, compared to 19 binary (and 3 ternary) mixtures for the 8-sensor MT-U array, attests to the value of the added sensors in the latter array. Seven of these 12 vapors were recognizable by both MT arrays at an $RR \geq 95\%$. The 5-sensor CAP array was capable of analyzing 11 of the 12 mixtures analyzed by the 5-sensor MT array.

In most cases the average RR (5– $10LOD$, RCR = 1:1) is higher for the MT array among these mixtures, but the differences are generally small. In all cases, the LOR_{95} with the MT array is at least as large as that with the ST array and is as much as 2-fold larger. However, a *t* test of the average LOR_{95} values from each array showed the difference not to be statistically significant. RCR_{10} values are comparable for the two arrays, though about 10% larger on average for the MT array. Interestingly, the largest RCR_{10} observed among these data is 36 (i.e., from 3:1 to 1:12), for the mixture of *n*-heptane + trichloroethylene (also seen for *n*-octane + trichloroethylene) with the 5-sensor MT array, which is somewhat larger than the largest RCR_{10} observed with the MT-U array. The extent of asymmetry observed is similar for both 5-sensor arrays and is comparable to that for the MT-U array. The strong correlations observed between values of *A* and the LOR-S product ratios for the MT-U array are also observed for the 5-sensor MT and ST arrays, as expected. The one marked difference between the ST and MT arrays is the lower LODs provided by the ST array (range = 30–160 ppm), which are generally about an order of magnitude lower than those of the MT array (range = 70–890 ppm). Thus, for the binary mixtures analyzed in this data set, the performance of ST and MT arrays is quite similar in most respects. The advantage in terms of LOR_{95} areas provided by the MT array is offset to some extent by the advantage of the ST array with regard to sensitivity.

CONCLUSIONS

A number of conclusions can be drawn from this study related to the use of MT arrays as detectors in microanalytical systems. First, above the LOD, the relative concentration ratios of the

vapors are much more important determinants of performance than are their absolute concentrations, and for binary mixtures the relative concentration range over which components can be reliably recognized is typically 5–20. When the purpose of the analysis is to determine all vapors in a complex mixture, this poses a significant constraint, because chromatographically unresolved binary mixture components at low relative concentrations cannot be detected reliably. The problem is even more severe for unresolved ternary mixtures. Furthermore, the analysis of binary (or ternary) mixtures whose components yield very different array sensitivities will be further constrained, favoring mixtures rich in the component for which the array is less sensitive. On the basis of the data generated here, if the concentration of the component to which the array is more sensitive exceeds that of the vapor to which the array is less sensitive by 2-fold or more, the minority component will not be detectable.

If, on the other hand, the purpose is to perform targeted-vapor analysis and the target vapor cannot be resolved from interfering compounds chromatographically, as long as the sensitivity to that vapor is greater than its coeluting interferences, it should be recognizable over a wide range of concentrations even if it is the minority component. If it is the majority component and present in 2-fold or greater excess, its recognition will be facilitated by the inability to detect the presence of the coeluting interference. Note, however, that quantification may be affected, since the presence of the interference, though not recognized, will contribute to the net response and thereby tend to positively bias estimates of target-vapor concentrations.

The impact on recognition of the inherent variability in the sensitivity and baseline noise of the sensors in the array was found to be quite significant. Without tight controls on the sources of variation in responses and response patterns, the advantages of using sensor arrays to confirm the identities of vapors eluting from an upstream chromatographic column at a particular retention time will be lost. In practice, this demands low-noise circuitry with drift compensation and minimizing fluidic and thermal variables that may affect sensor responses directly or indirectly, such as through the delivery of samples to the sensor array.

The brief comparison of 5-sensor MT and ST arrays performed here with respect to LOR values revealed that the general behavior is quite similar to that of the 8-sensor MT array in terms of the range of recognizable compositions and the degree of asymmetry. As expected, the 5-sensor MT array provided somewhat larger LOR_{95} values, but the sensitivity advantage of the ST array was a notable extenuating factor.

This is only the second report to consider the systematic analysis of mixtures by arrays of microsensors using the LOR. This metric of performance permits detailed insights into array performance. The magnitude of the LOR facilitates ranking mixtures in terms of the ease with which they can be recognized and differentiated from their constituents and identifying mixtures where such discriminations are not possible. As the trend toward an increasing emphasis on mixture analyses with microsensor arrays continues, this metric should find wider application.

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