Detection of Volatile Organic Compounds in Gasoline and Diesel Using the zNose®

Edward J. Staples, Electronic Sensor Technology

Electronic Noses

An electronic nose produces a recognizable response based upon the chemical composition of an odor, aroma, or vapor. A new type of electronic nose, called the zNose®, uses ultra-fast gas chromatography to simulate an almost unlimited number of specific virtual chemical sensors, and produces olfactory images based upon aroma chemistry. The zNose® is able to perform analytical measurements of volatile organic vapors and odors in near real time with part-per-trillion sensitivity. Separation and quantification of the individual chemicals within an odor is performed in seconds. Using a patented solid-state mass-sensitive detector, picogram sensitivity, universal non-polar selectivity, and electronically variable sensitivity is achieved. An integrated vapor preconcentrator coupled with the electronically variable detector, allow the instrument to measure vapor concentrations spanning 6+ orders of magnitude.

This paper describes use of a portable zNose® (Figure 1) to quantify the concentration of volatile organic compounds in gasoline and diesel samples taken from six different service stations. Variations in chemical composition and visual olfactory images enable the instrument to quickly detect mixing of octanes and adulterated fuels.

Figure 1- Portable zNose® technology incorporated into a handheld instrument

How the zNose™ Quantifies the Chemistry of Vapors

A simplified diagram of the zNose™ system is shown in Figure 2. The system consists of two sections. One uses helium gas, a capillary tube (GC column) and a solid-state detector. The other section consists of a heated inlet and a pump which samples ambient air. Linking the two sections is a "loop" trap, which acts as a preconcentrator when placed in the air section (sample position) and as an injector when placed in the helium section (inject position).   Operation is a two step process. Ambient air (vapor) is first sampled and organic vapors collected (preconcentrated) on the trap.   After sampling the trap is switched into the helium section where the collected organic compounds are injected into flowing helium gas. The organic compounds pass through a capillary column with different velocities and thus individual chemicals exit the column at specific times. As they exit the column they are detected and quantified by a solid state detector.

An internal high-speed gate array microprocessor controls the taking of sensor data which is transferred to a user interface or computer using an RS-232 or USB connection. Odor chemistry, shown in Figure 3, can be displayed as a sensor spectrum or a polar olfactory image of vapor intensity vs retention time.   Calibration is accomplished using a single n-alkane vapor standard. A library of retention times of known chemicals indexed to the n-alkane response (Kovats indices) allows for machine independent measurement and compound identification.
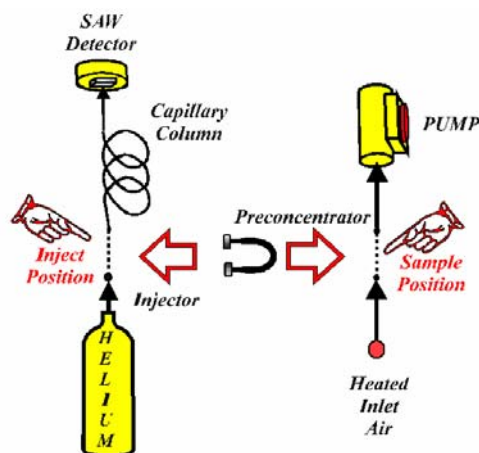
Figure 2- Simplified diagram of the zNose™ showing an air section on the right and a helium section on the left. A loop trap preconcentrates organics from ambient air in the sample position and injects them into the helium section when in the inject position.
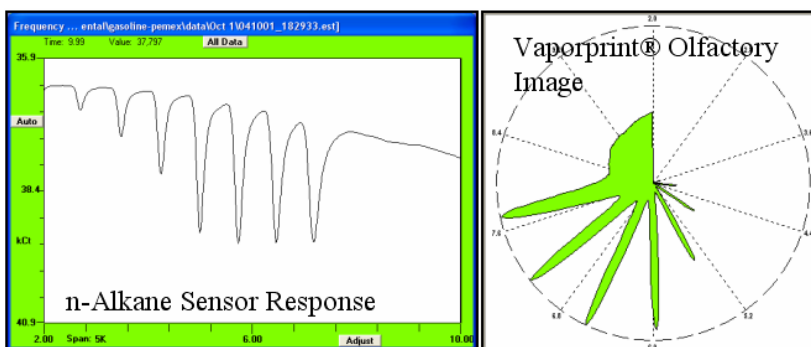
Figure 3- Sensor response to n-alkane vapor standard, here C7-C14, can be displayed as sensor output vs time or its polar equivalent olfactory image.

Chemical Analysis (Chromatography)

The time derivative of the sensor spectrum (Figure 3) yields the spectrum of column flux, commonly referred to as a chromatogram. The chromatogram response (Figure 4) of n-alkane vapors (C7 to C14) provides a relative measure of retention time. Graphically defined regions, shown as red bands, calibrate the system and provide a reference time base against which other chemical responses can be compared or indexed. As an example, a peak midway between C10 and C11 would have a retention index of 1050.
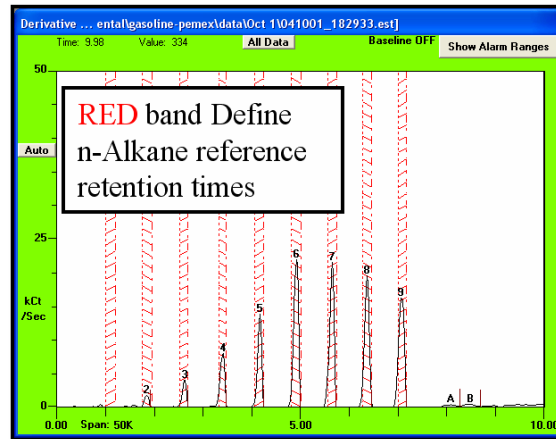

Figure 4 - Chromatogram of n-alkane vapors C6 to C14).

Chemical Composition of Vapors from Gasoline

Blended gasolines contain a large number of volatile organic compounds. A list of the most volatile elements and their boiling points is shown in Table I. A plot of boiling points relative to n-alkanes, Figure 6, simulates the anticipated chromatogram response for these compounds. Although the octane rating of blended gasolines from different producers may be equivalent, the chemistry can be very different and some blends are reported to contain over 150 different compounds.

Table 1 -Boiling point of volatile organic compounds in gasoline

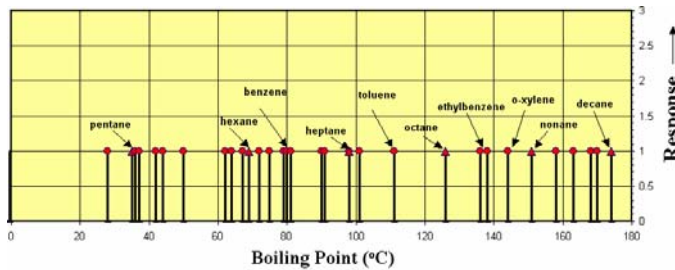| Compound	Boiling Point
n-butane	-0.5
n-pentane	35
n-hexane	69
n-heptane	98
n-octan	126
2-methylpropane	-12
2-methylbutane	28
2-methylpentane	62
3-methylpentane	64
2-methylhexane	90
3-methylhexane	91
2,2-dimethylpentane	79
2,2,3-trimethylbutane	81
2,2,4-trimethylpentane	98
cyclopentane	50
methylcyclopentane	72
cyclohexane	81
methylcyclohexane	101
benzene	80
toluene	111
ethylbenzene	136
m-xylene	138
p-xylene	138
o-xylene	144
3-ethyltoluene	158
1,3,5-trimethylbenzene	163
1,2,4-trimethylbenzene	168
2-pentene	37
2-methylbutene-2	36
2-methylpentene-2	67
cyclopentene	44
1-methylcyclopentene	75
1,3 cyclopentadiene	42
dicyclopentadiene	170

Figure 5- Boiling point of chemicals within gasoline are used to simulate chromatogram response.

Gasoline and Diesel Samples

For evaluation purposes samples of Pemex gasoline (87 and 92 octane) were taken from six different service stations. Samples of diesel were also taken from five different service stations. Samples were kept in a sealed 40 milliliter vials until tested.

GC Methods and Testing Procedures

Sample Preparation

Gasoline and diesel fuels were tested using (1) fully vaporized samples and (2) headspace vapors above liquid samples. Fully vaporized samples were prepared by injecting 2 µliters of sample into a sealed 250 milliter bottle. Headspace testing of vapors from liquid fuel used 3 milliliters of sample in a sealed 40 milliter vial.

Sample Preconcentration Time

The concentration of vapor samples from gasoline and diesel were high enough that only a small sample volume, typically 1-0.5 milliliter, was required. Vapor samples were acquired using the internal sampling pump and preconcentrator of the zNose®. Sample times were typically 2-5 seconds depending upon the detector sensitivity setting and column temperature programming.

Column Ramping

A db624 column was used and temperature ramping rates could be varied from zero (isothermal) to as high as 18°C/second. Three basic temperature profiles were used 10°C/second, 5°C/second, and 3°C/second. Column starting temperature was 40°C and ending temperature was 140°C. For quick screening a high ramping rate was used while for better resolving power (peak separation) a lower ramping rate was more appropriate.

Detector Response (Temperature)

The sensitivity of a surface acoustic wave detector is dependent upon the temperature of the sensing crystal surface. For optimum response to the most volatile compounds, such as benzene, a detector temperature of 10°C was used. For testing of high conconcentration headspace vapors a detector temperature of 40°C to 60°C was used. Sensitivity was adjusted to provide optimum signal to noise without overloading.

Calibration Standards

Calibration standards were made by injecting known concentrations of benzene, toluene, ethylbenzene, o-xylene, and n-alkanes into septa sealed 40 milliter vials and 250 milliter bottles. Vapor standards were used to verify system linearity and to provide reference retention times for indexing peak retention times.

Standard Deviation

The standard deviation of replicate measurements using vapor standards was typically 1-5% . As an example, three vapor standards were prepared by injecting 2 μliters of gasoline from a single sample into three 250 milliliter bottles. Test results shown in figure 6 show standard deviation between bottles to be less than 5% for all analytes below C10. Higher boiling point compounds (>C10) showed higher standard deviation as a result of condensation on the walls of the bottles and in the room temperature sample needle.
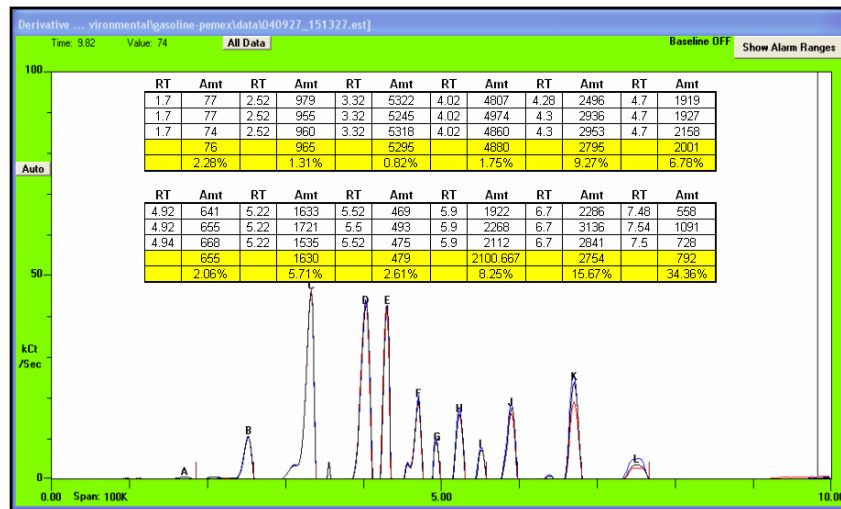

Figure 6- Standard deviation of three vapor samples prepared from a single source.

Linearity of Response

Calibration standards using BTEX were used to test system linearity for vapor concentrations up to approximately 50 ppm. Results, shown in Figure 7, showed excellent linearity:

R^2(o-xylene) = 0.99

R^2(ethylbenzene) = 0.992

R^2(toluene) = 0.996
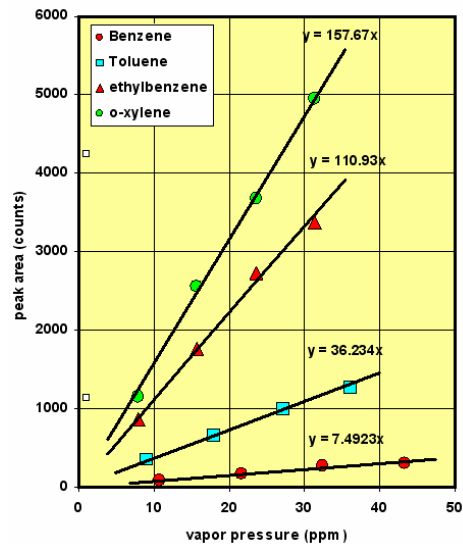
R^2(benzene) = 0.961

Figure 7- Linear BTEX response using 10°C detector, 2 sec sample time and 5°C/sec ramp rate.

Testing of Fully Vaporized Gasoline and Diesel Samples
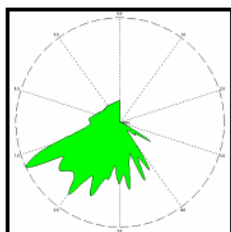
<u>Chromatography Comparisons</u>

Gasoline and diesel samples were compared by fully vaporizing 2 µliters of each fudl sample in a 250 milliter bottle. Vapor within the bottle was sampled using a side-ported needle attached to the inlet of the zNose® as shown in Figure 8.

Illustrating two different GC methods, replicate measurements on vapors from a bottle containing vapors from an 87-octane gasoline sample are shown in figure 9. Method 1 used a 10^oC/second column ramp rate and produced a 10-second chromatogram while method 2 used a 5^oC/second column

Figure 8- Direct sampling of fully vaporized gasoline samples with zNose®

ramp which produced a 20-second chromatogram. Also shown are olfactory images generated by the two methods. Olfactory images, although not strictly quantitative, allow operators to quickly assess the overall chemical response produced by a chemical vapor. Often differences between vapors can be more easily seen in olfactory images rather than chromatograms.
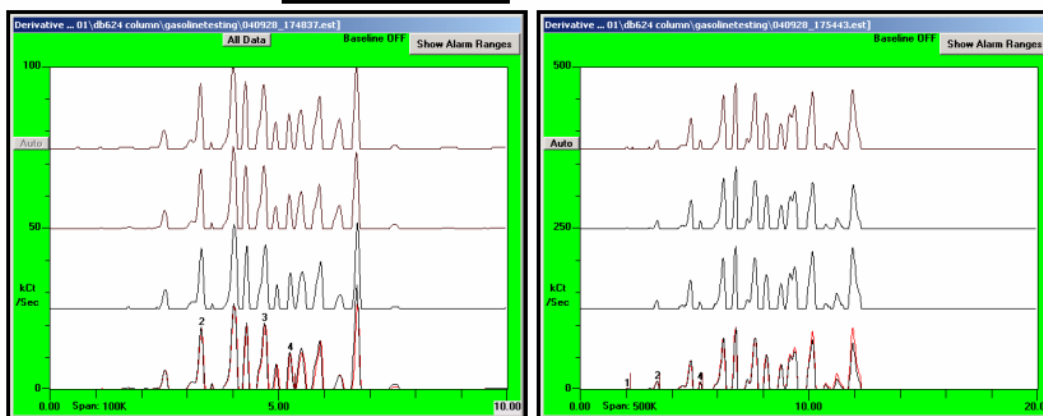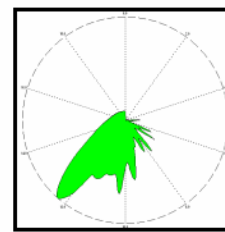

Figure 9- Replicate measurements taken on 87-octane gasoline vapors using two different GC methods.

Although a chemical analysis cannot determine the octane rating of blended gasoline it can be used to distinguish between different octane-rated blends. As an example, vertically offset chromatorams of 87 and 92 octane gasoline samples from three different service stations are shown in Figure 10. Using six virtual chemical sensors (denoted by red bands), the concentration of specific chemicals can be tabulated and compared. In this case (Pemex), the concentration of the peak "gas-1250" can be used to distinguish between 87 and 92 octane rated gasoline.

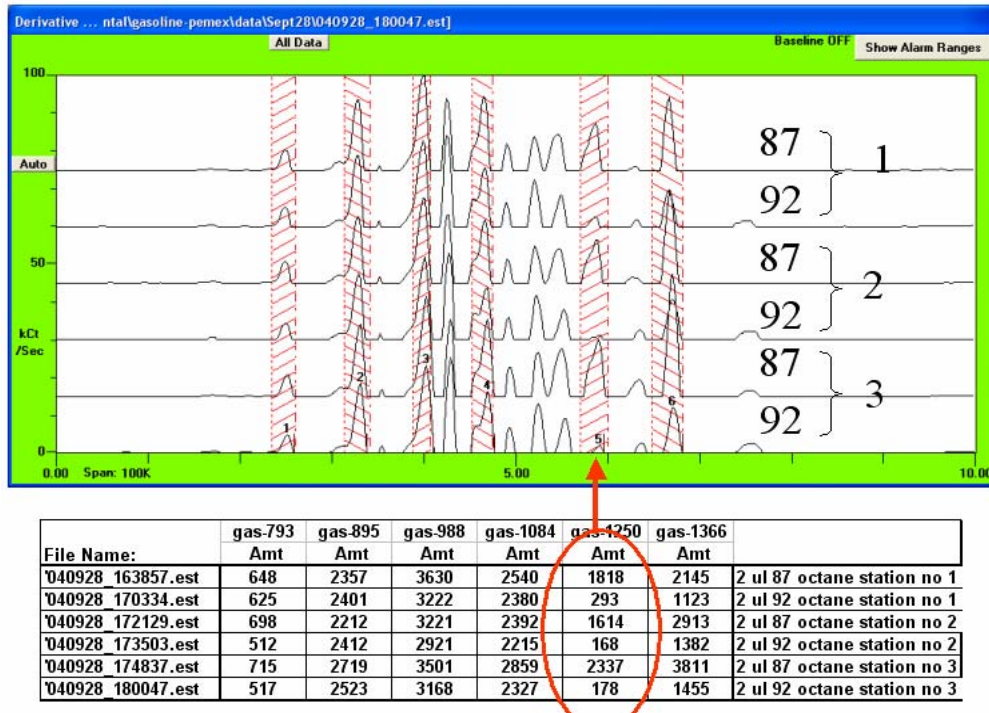| File Name:	gas-793 Amt	gas-895 Amt	gas-988 Amt	gas-1084 Amt	gas-1250 Amt	gas-1366 Amt	
'040928_163857.est	648	2357	3630	2540	1818	2145	2 ul 87 octane station no 1
'040928_170334.est	625	2401	3222	2380	293	1123	2 ul 92 octane station no 1
'040928_172129.est	698	2212	3221	2392	1614	2913	2 ul 87 octane station no 2
'040928_173503.est	512	2412	2921	2215	168	1382	2 ul 92 octane station no 2
'040928_174837.est	715	2719	3501	2859	2337	3811	2 ul 87 octane station no 3
'040928_180047.est	517	2523	3168	2327	178	1455	2 ul 92 octane station no 3

Figure 10- Vertically offset chromatograms showing differences between 87 and 92-octane rated gasoline samples from stations 1,2, and 3.

Replicate measurements on vapor samples of gasoline from six different service stations using Method 1 and 2 were performed and averaged peak concentrations in counts are tabulated in Figures 11 and 12. Peaks are identified by their Kovats indices e.g. gas-1250 has an index of 1250.

10ps2a1b Method 1

File Name:	gas-793 Amt	gas-895 Amt	gas-988 Amt	gas-1084 Amt	gas-1250 Amt	gas-1366 Amt	
'040928_163857.est	648	2357	3630	2540	1818	2145	2 ul 87 octane station no 1
'040928_170334.est	625	2401	3222	2380	293	1123	2 ul 92 octane station no 1
'040928_172129.est	698	2212	3221	2392	1614	2913	2 ul 87 octane station no 2
'040928_173503.est	512	2412	2921	2215	168	1382	2 ul 92 octane station no 2
'040928_174837.est	715	2719	3501	2859	2337	3811	2 ul 87 octane station no 3
'040928_180047.est	517	2523	3168	2327	178	1455	2 ul 92 octane station no 3

Substance: File Name:	gas-793 Amt	gas-895 Amt	gas-988 Amt	gas-1084 Amt	gas-1250 Amt	gas-1366 Amt	Notes:
'040929_102111	699	2296	3447	2572	1962	2640	2 ul 87 octane station no 4
'040929_103516	559	2441	3156	2272	66	885	2 ul 92 octane station no 4
'040929_133402	704	2546	3130	2332	1574	2624	2 ul 87 octane station no 5
'040929_135556	577	2496	3200	2285	168	1319	2 ul 92 octane station no 5
'040929_140808	639	2690	3423	2621	2118	3628	2 ul octane 87 station no 6
'040929_142434	557	2516	3124	2114	138	1468	2 ul 92 octane station no 6

Figure 11- Summary of peak concentrations using Method 1 to measure vapors of 87 and 92- octane rated gasoline samples from six different service stations.

5ps2a1b Method 2

File Name:	gas-793 Amt	gas-895 Amt	gas-988 Amt	gas-1084 Amt	gas-1250 Amt	gas-1366 Amt	
'040928_164613.est	1810	8069	16796	15056	12322	9842	2 ul 87 octane station no 1
'040928_170842.est	1790	8446	14860	16691	1471	3585	2 ul 92 octane station no 1
'040928_172603.est	1949	7848	14904	13218	10863	15023	2 ul 87 octane station no 2
'040928_173936.est	1640	8138	14529	17690	386	4651	2 ul 92 octane station no 2
'040928_175443.est	1884	8360	17316	17289	18651	19046	2 ul 87 octane station no 3
'040928_180652.est	1529	9029	15319	20158	681	5803	2 ul 92 octane station no 3

Substance: File Name:	gas-793 Amt	gas-895 Amt	gas-988 Amt	gas-1084 Amt	gas-1250 Amt	gas-1366 Amt	Notes:
'040929_102553	1928	8206	15971	14366	12026	10714	2 ul 87 octane station no 4
'040929_103950	1645	7851	14375	15687	458	3201	2 ul 92 octane station no 4
'040929_134019	1947	8246	14711	12295	9160	11730	2 ul 87 octane station no 5
'040929_140033	1704	8193	14416	15817	1108	4691	2 ul 92 octane station no 5
'040929_141619	1858	7729	16280	15601	15728	19972	2 ul 87 octane station no 6
'040929_142916	1649	8387	14540	17484	608	5277	2 ul 92 octane station no 6

Figure 12- Summary of peak concentrations using Method 2 to measure vapors of 87 and 92-octane rated gasoline samples from six different service stations

Olfactory Image Comparisons

Olfactory images (VaporPrints®) provide a pattern which can be used to recognize different blends of Pemex gasoline. Examples of images using the two previous GC methods are shown in Figure 13. The promenent bulge on the lower left side of images for 87-octane gasoline is clearly different from the images for 92-octane gasolines.
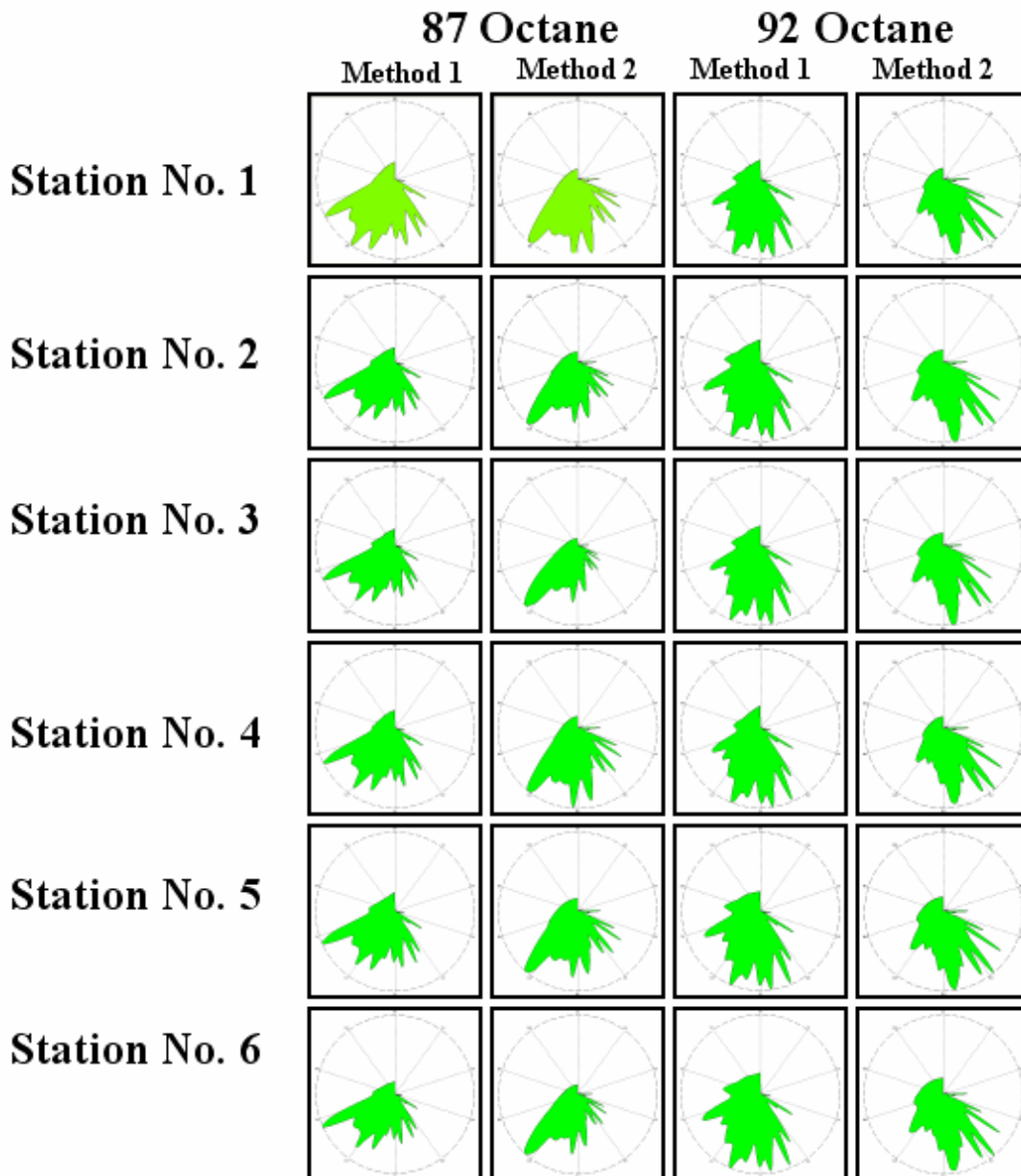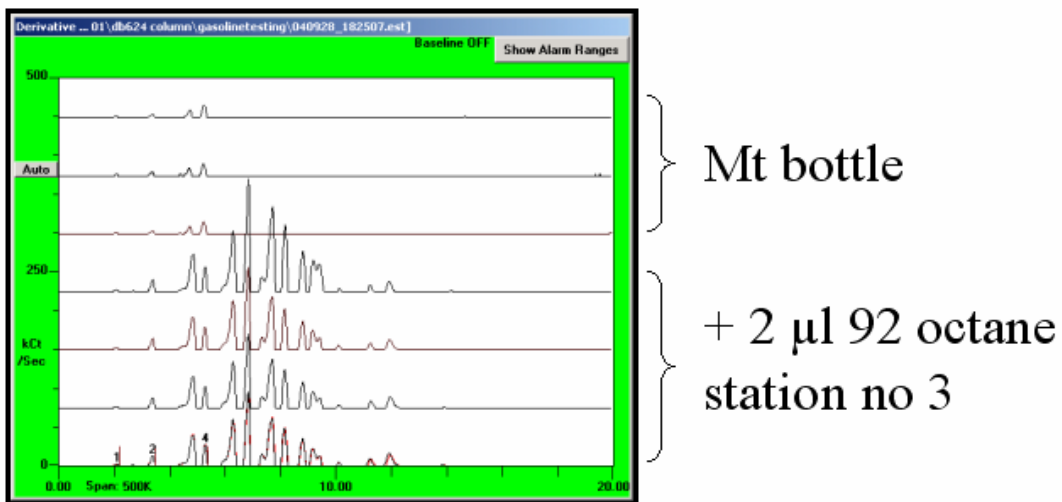

Figure 13- Olfactory images form visual patterns which can be used to characterize the overall vapor chemistry of blended gasoline and to distinguish between different blends.

Response to Addition of BTX to Gasoline Samples

Adding known amounts of benzene, toluene, and o-xylene to gasoline vapors and measuring the increase in concentration simulates the effects of adulteration of gasoline and also enables the concentration of these compounds in the gasoline to be indirectly measured. A 250 mL bottle containing 69 nanograms/milliliter BTE was first measured and then 2 µliters of 92 octane rated gasoline was added. The vertically offset chromatograms and the resulting peak concentration counts are tabulated in Figure 14. Using the average of replicate chromatograms the response factors for benzene, toluene, and o-xylene were 2.29, 8.55, and 33.04 counts/ng/mL respectively. Adding 2 µliters of gasoline to the bottle increased the amount of each compound by 66.8, 177.5, and 39.7 ng/mL respectively. Using the volume of the bottle and assuming a density for gasoline of 1, the amount of benzene, toluene, and o-xylene in the gasoline is calculated to be approximately 0.84%, 2.22%, and 0.5% respectively.

	benzene Counts	toluene Counts	xylene counts	
040928_181600.est	151	602	2313	8 ul btex
040928_181731.est	167	574	2181	8 ul btex
040928_181903.est	156	595	2346	8 ul btex
Average	158	590	2280	8 ul btex
040928_182034.est	329	2291	4034	8 ul btex + 92 octane station no 3
040928_182205.est	286	2067	3519	8 ul btex + 92 octane station no 3
040928_182337.est	304	2026	3446	8 ul btex + 92 octane station no 3
040928_182507.est	324	2047	3369	8 ul btex + 92 octane station no 3
Average	311	2108	3592	8 ul btex + 92 octane station no 3

Figure 14- Adding gasoline to BTX vapor standard simulates adulteration and allows the concentration of BTX in gasoline to be calculated.

Mixed Gasoline Samples

A common form of gasoline adulteration is to add 87-octane gasoline to 92-octane rated gasoline. Replicate chromatograms of vapors from 92-octane (left), 87-octane (right), and a 50% mixture (center) are shown in Figure 15. Tabulating the concentrations of the six principal components and using the concentration of peak "gas-1250", the concentration of the mixture is calculated to be 55%. Mixing of different octanes can be measured with an accuracy of plus or minus 5%.

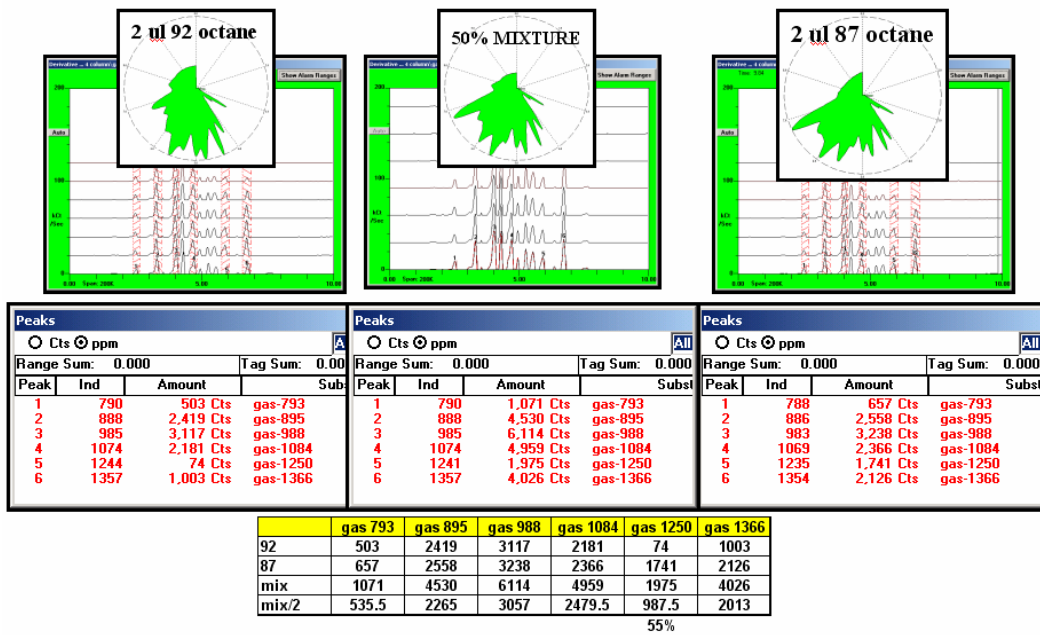|	gas 793	gas 895	gas 988	gas 1084	gas 1250	gas 1366
92	503	2419	3117	2181	74	1003
87	657	2558	3238	2366	1741	2126
mix	1071	4530	6114	4959	1975	4026
mix/2	535.5	2265	3057	2479.5	987.5	2013
					55%	

Figure 15- Mixing Pemex gasoline of different octane ratings can be measured by the concentration of gasoline compound peak with an index of 1250 e.g. "gas-1250".

Chromatography and Octane Rating

Illustrating why a chemical analysis cannot be used to determine the octane rating of gasoline, chromatograms of identically rated gasoline produced by Pemex and Exon-Mobile (Florida) are overlaid for comparison in figure 16. It is clear that the chemistry is not unique and that more than one blend of chemicals can produce the same octane rating.
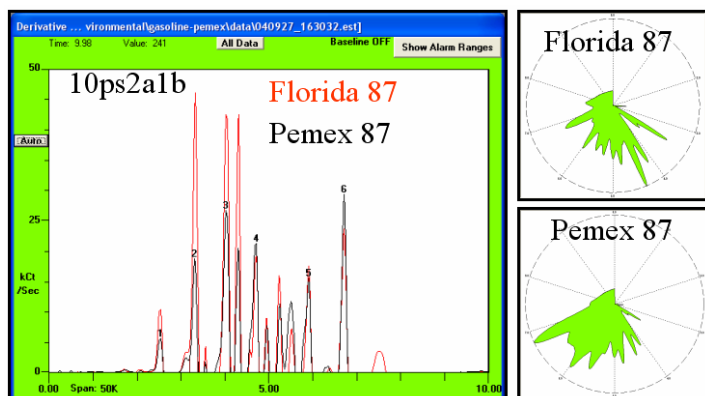

Figure 16- 87-octane rated gasoline from different producers.

Comparison of Fully Vaporized Diesel Samples

The chemistry of diesel samples taken from five Pemex service stations as well as from a US (Florida) producer are shown in Figure 17. Diesel contains mainly n-alkanes and the concentration of these compounds are tabulated for comparison. The Pemex diesel samples were quite uniform with the exception of station number 5. Comparison with gasoline chromatograms revealed that this sample is actually gasoline.

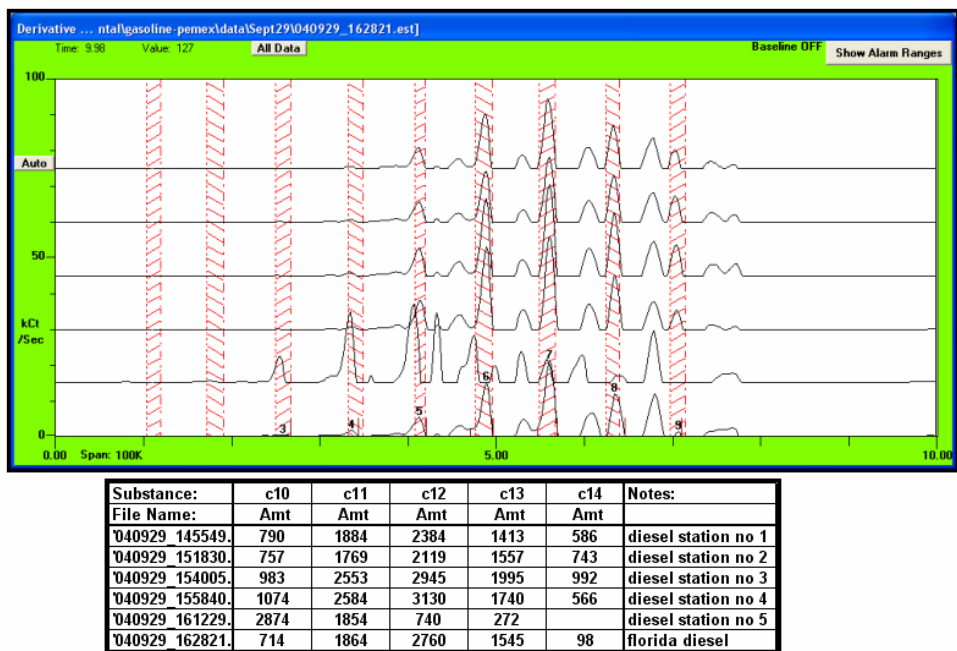| Substance:	c10	c11	c12	c13	c14	Notes:
File Name:	Amt	Amt	Amt	Amt	Amt	
'040929_145549.	790	1884	2384	1413	586	diesel station no 1
'040929_151830.	757	1769	2119	1557	743	diesel station no 2
'040929_154005.	983	2553	2945	1995	992	diesel station no 3
'040929_155840.	1074	2584	3130	1740	566	diesel station no 4
'040929_161229.	2874	1854	740	272		diesel station no 5
'040929_162821.	714	1864	2760	1545	98	florida diesel

Figure 17- Vertically offset chromatograms of vapors of diesel samples from five different service stations and tabulation of principal alkane compound concentrations.

Comparison of the above diesel samples using olfactory images is shown in Figure 18 and the image of the sample from station number 5 is easily recognized as gasoline. Tabulated alkane peak concentrations for the diesel samples from different stations are shown in Figure 19. The chemistry of vapors from the diesel samples from the different service stations was consistent and there were no significant variations.
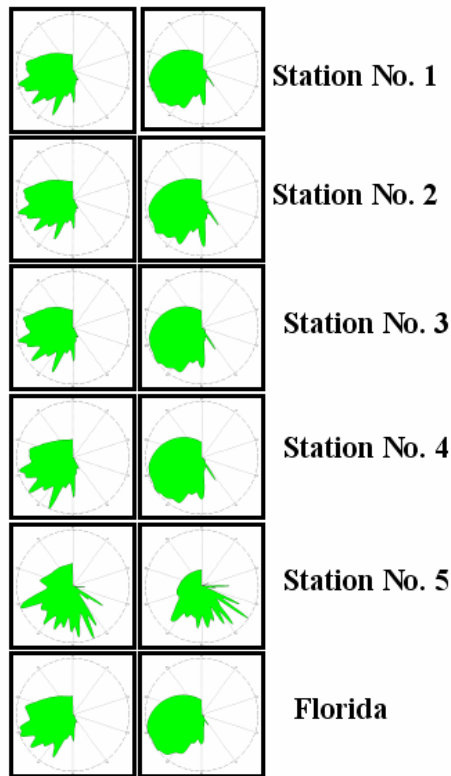
Figure 18- Olfactory images from diesel samples

Diesel method 1

Substance:	c10	c11	c12	c13	c14	Notes:
File Name:	Amt	Amt	Amt	Amt	Amt	
'040929_145549.	790	1884	2384	1413	586	diesel station no 1
'040929_151830.	757	1769	2119	1557	743	diesel station no 2
'040929_154005.	983	2553	2945	1995	992	diesel station no 3
'040929_155840.	1074	2584	3130	1740	566	diesel station no 4
'040929_161229.	2874	1854	740	272		diesel station no 5
'040929_162821.	714	1864	2760	1545	98	florida diesel

Diesel method 2

Substance:	c10	c11	c12	c13	c14	Notes:
File Name:	Amt	Amt	Amt	Amt	Amt	
'040929_150033.	3701	17154	26300	18340	5644	diesel station no 1
'040929_153039.	3653	14265	18099	11474	3345	diesel station no 2
'040929_154655.	5152	31276	41430	21532	4423	diesel station no 3
'040929_160314.	5110	34864	46566	21200	4002	diesel station no 4
'040929_161706.	13698	4639	2283	1637		diesel station no 5
'040929_163256.	3123	13545	29808	24274	3663	florida diesel

Figure 19- Tabulated peak concentrations from diesel samples using two different GC methods.

Direct Sampling of Headspace Vapors

The chemical composition of vapors above the surface of liquid fuel samples reflect the chemical composition of the fuel itself. The effect is described by Henry's Law. The ratio of vapor-to-liquid concentration is a constant which is dependent upon the solubility and the vapor pressure of each chemical. Measuring the headspace vapors above gasoline and diesel samples is simpler than preparing vapor samples, however, because concentrions are temperature sensitive, standards and unknown samples must be held at a constant temperature for accurate comparisons.

The chemical composition of head-space vapors produced by 3 milliliters of liquid phase gasoline placed in a 40-milliliter vial was measured by inserting the sampling needle of the zNose® into the headspace as shown in Figure 20.

Figure 20- Direct sampling of gasoline and diesel headspace vapors with the zNose®.

Vertically offset chromatograms for headspace vapors from 87-octane gasoline from the six service station samples is shown in Figure 21. The peak area (concentration) for the six principal components (marked by red bands) of the gasoline are shown in the accompanying bar chart. Uniformity between the samples was very good. Vapors from gasolines with this octane rating displayed a recognizeable pattern involving peaks 3,4,and 5..
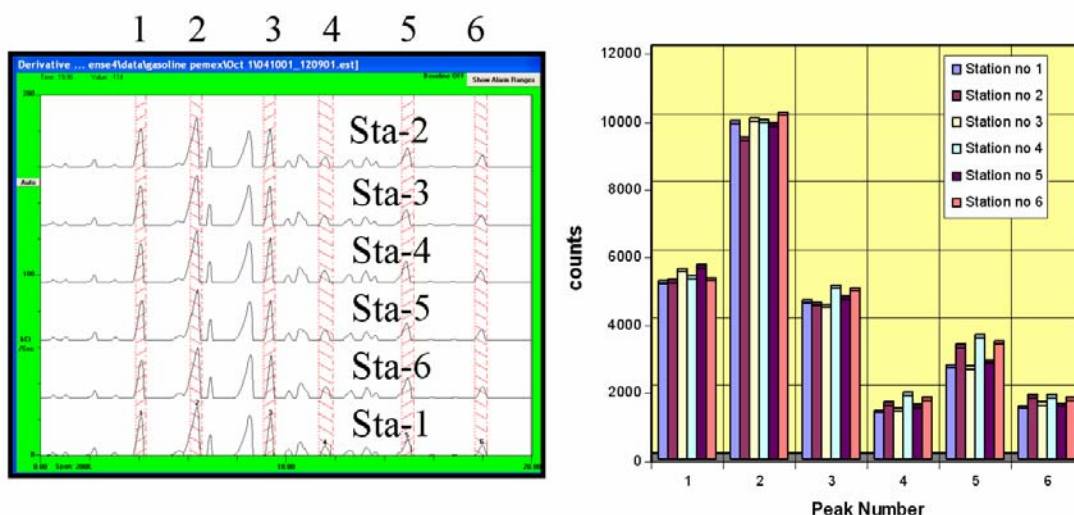

Figure 21- Analysis of headspace samples of 87-octane gasoline supplied by six different service stations. The concentration of six principal chemicals formed a recognizable pattern.

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Vertically offset chromatograms for headspace vapors from 92-octane gasoline from the six service station samples is shown in Figure 22. The concentration of the same six principal components in 92-octane gasoline shown in the accompanying bar chart was very different from that of 87-octane gasoline and the different blends could easily be recognized by the relative concentration of peaks 4,5, and 6.
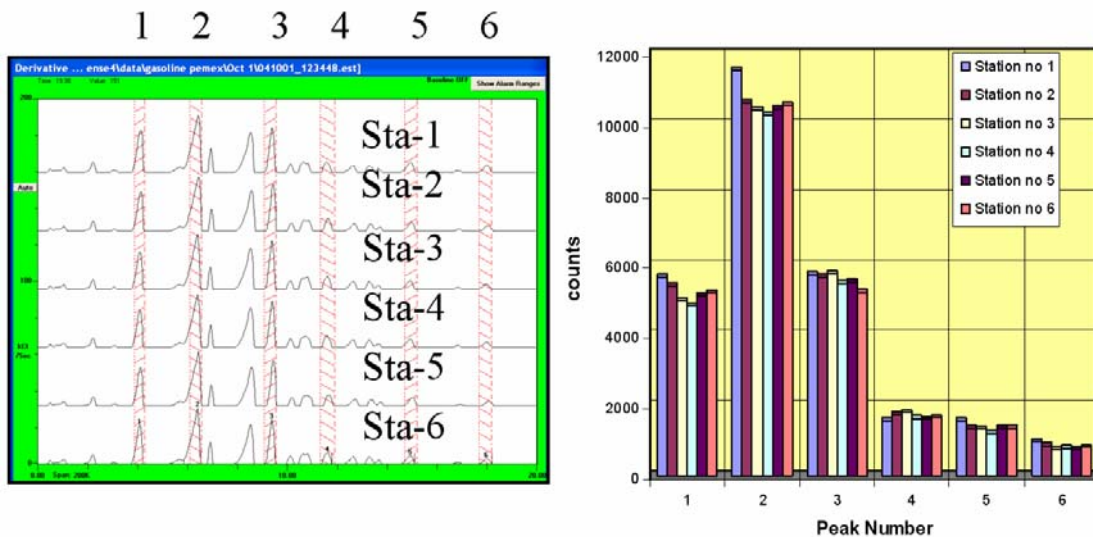

Figure 22- Analysis of headspace samples of 92-octane gasoline supplied by six different service stations. The concentration of six principal chemicals forms a recognizable pattern.

Vertically offset chromatograms for headspace vapors from diesel from four service station samples is shown in Figure 23. The concentration of the five principal components in diesel are shown in the accompanying bar chart. Samples from stations 3 and 4 had higher headspace concentrations of C10 and C11 alkanes than samples from stations 1 and 2.
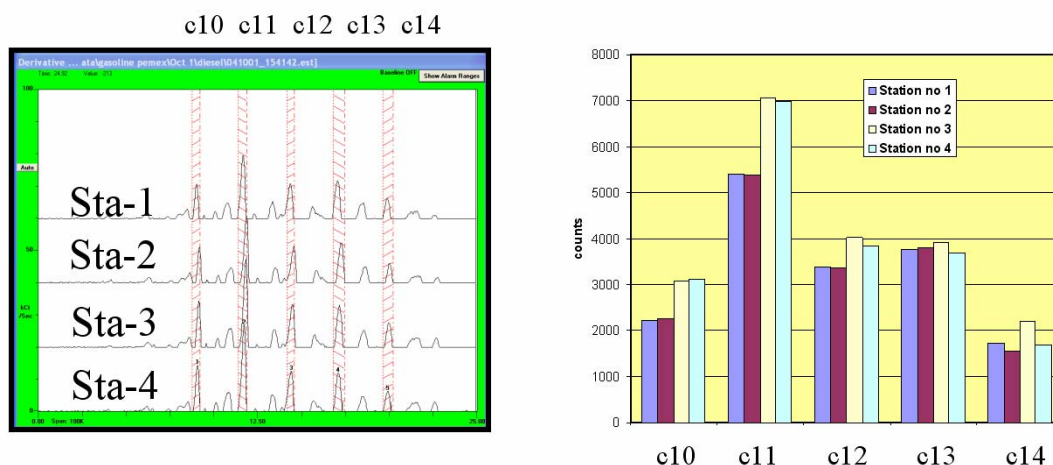

Figure 23- Analysis of headspace samples of diesel supplied by four different service stations. The concentration of n-alkanes forms a recognizable pattern.

Comparing Olfactory Images of Headspace Vapors

Olfactory images of headspace vapors for 87 and 92-octane gasoline samples from each of the six service station are shown in Figure 24. Very little difference can be seen between images from the different stations. However, the difference between octane-rated blends can clearly been seen in the size of peaks along the top-left portion of the images.
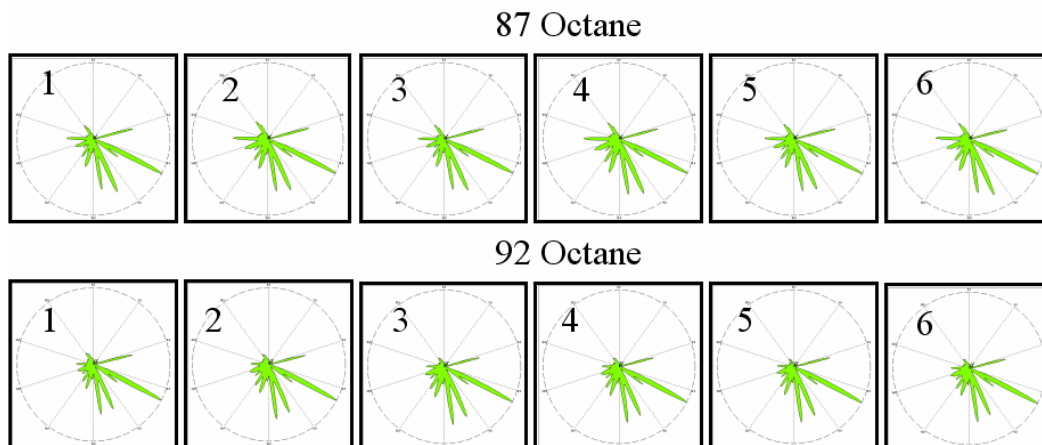

Figure 24- Olfactory images of headspace vapors from 87 and 92-octane gasoline samples.

Olfactory images of headspace vapors for diesel samples from each of the five service station are shown in Figure 25. Only minor differenes are seen in the images from stations 1-4 but the image of the sample from station number 5 is clearly gasoline and not diesel. Comparing the station-5 image of Figure 25 with the images for 87 and 92-octane blends in Figure 24 suggests that this is an adulterated gasoline sample because it does not match the image of either blend.
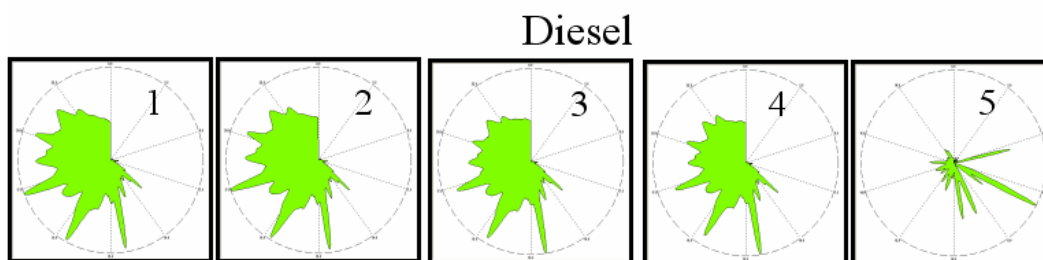

Figure 25- Olfactory images of headspace vapors from diesel samples.

Headspace Vapors from Adulterated Gasoline

The 'diesel' sample from station number 5 was clearly gasoline and not diesel. As noted from comparison of olfactory images it was different from pure 87 or 92-octane gasoline blends. The differences are more clearly seen in the overlaid chromatograms from 87 and 92-octane blends shown in Figure 26. Mixing is evident in peak number 5 (998 counts). Interpolating between 87 and 92-octane counts shows that the station 5 sample is actually a mix of 63% 92-octane and 37% 87-octane gasolines. Also, the addition of toluene (A) and an unidentified compound (B) with an index of 735 is detected. A more detailed comparison of the volatile compounds is shown in Figure 27.
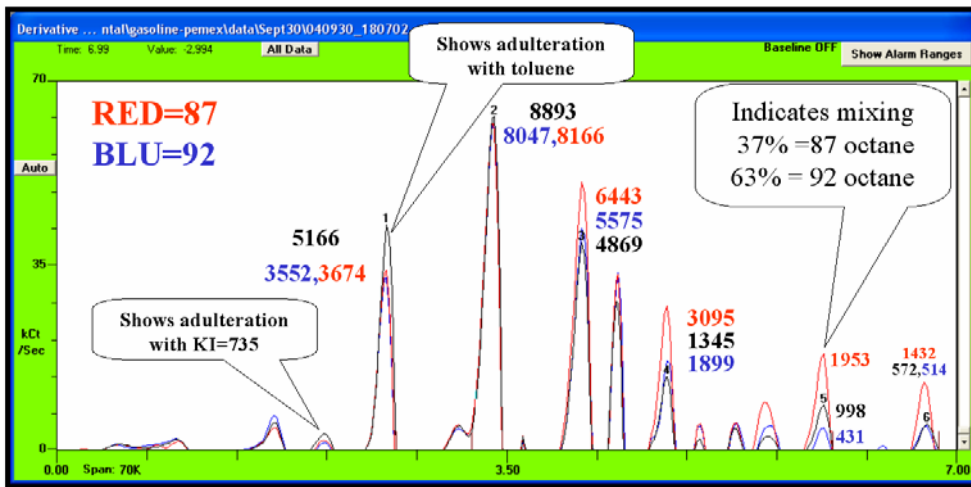

Figure 26- Adulterated gasoline headspace vapors with 87 and 92-octane chromatograms over-laid for comparison. Peak area counts are also shown for comparison.
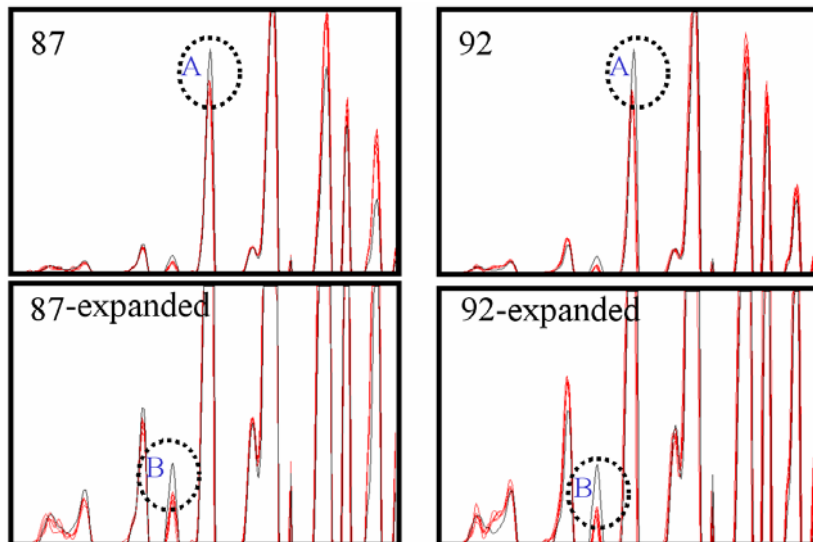

Figure 27- Detailed views of chromatograms showing adulteration by addition of volatile organics in gasoline sample from station number 5.

Summary

Screening and quantification of the odor chemistry of volatile organics such as gasoline and diesel fuel is fast and easy using the portable zNose®.   Due to their high volatility, detecting chemical vapor concentrations well into the part-per-trillion range is possible. Because screening is based upon high speed gas chromatography, on-site screening results can easily be compared and validated by independent laboratory testing.

Gasoline and diesel samples from multiple service stations were tested and compared using headspace vapors from liquid samples as well as sealed bottles containing fully vaporized fuel samples. In both cases comparable results were achieved and the zNose® was able to differentiate between different octane blends and to detect mixing of different octanes and adulteration using ultra-fast 10-second chromatograms and olfactory images called Vaporprints®. Sampling of headspace vapors from liquid fuel samples offers the most direct method because minimal sample preparation is required.

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