A QUICK EVALUATION OF GASOLINE VAPORS USING THE zNOSE™

System Description

The zNose™ is an entirely new electronic nose because it uses flash chromatography and not an array of dissimilar sensors. The zNose™ is produced in two configurations, a handheld module, Figure 1, and a benchtop model. Both have identical performance and can separate and quantify the concentration of volatile organics over the hydrocarbon range C6-C30 in 10 seconds. The zNose™ is equipped with an internal He carrier gas tank allowing over 300 vapor samples to be analyzed without refilling. With the zNose™ different chromatography columns can be used to optimize the speciation process. For comparison, in our testing of gasoline, a dB-5 and a dB-624 capillary column were used. The dB-624 nominally gave better speciation on volatile compounds whereas the dB-5 column was able to better speciate high molecular weight compounds.

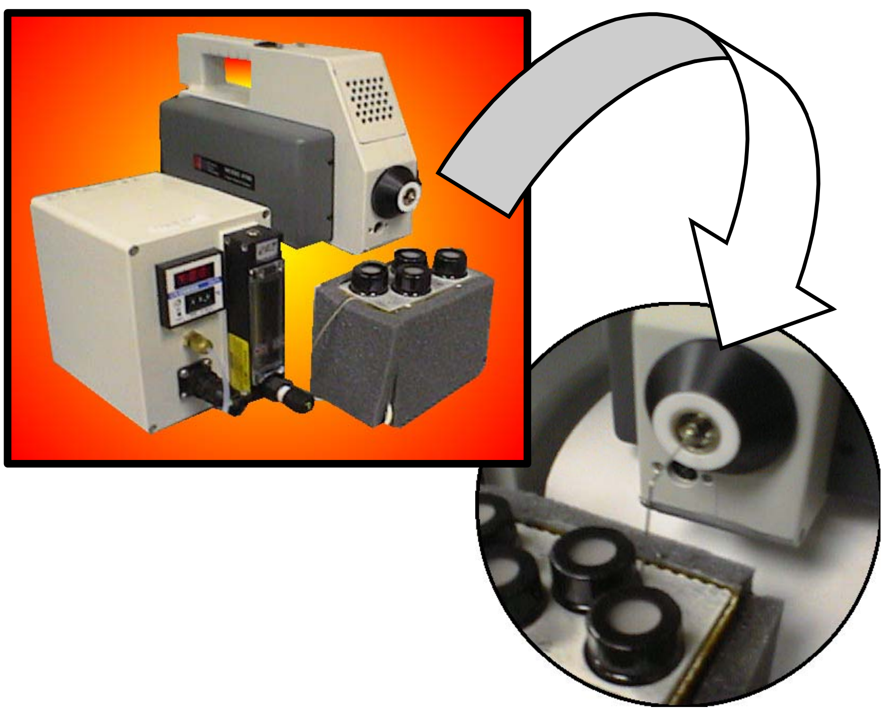


Figure 1- Model 4100 zNoseTM is handheld and attached to a support case by means of an eight-foot unbiblical cable. This allows for maximum flexibility in performing remote vapor measurements. Here the zNose is seen together with the model 3100 vial heater controller.

The patented SAW detector used in the zNose™ is non-polar and is universally selective to all compounds and inversely proportional to their vapor pressure. The sensitivity of the SAW detector can be electronically controlled over three orders of magnitude with picogram sensitivity being achieved on the highest setting. Vapor sampling with the zNose™ is accomplished with an internal sampling pump and Tenax© preconcentrator. Test sample volume (0.5 cc to 150 cc) is determined by selection of preconcentration time (1 to 300 seconds). These controls allow the zNose™ to measure vapor concentrations spanning over 6 orders of magnitude.

The main features of the zNose™ are illustrated in Figure 2 where a mixture of fully saturated n-alkanes has been used to create a test vapor. The sensor signal is a frequency proportional to the amount of each compound's mass as it exits the GC column. A chromatogram (column flux vs time) is produced by taking the derivative of the sensor signal. The peak in column flux for that analyte defines the retention time of each alkane. The zNose™ can detect, quantify, and list the concentration of each analyte using these signals. In addition, a virtual chemical sensor array can be created and used to monitor just those compounds selected by the user. Alternately, an olfactory image of the entire odor, smell, or fragrance can be created in a polar display of the sensor signal.

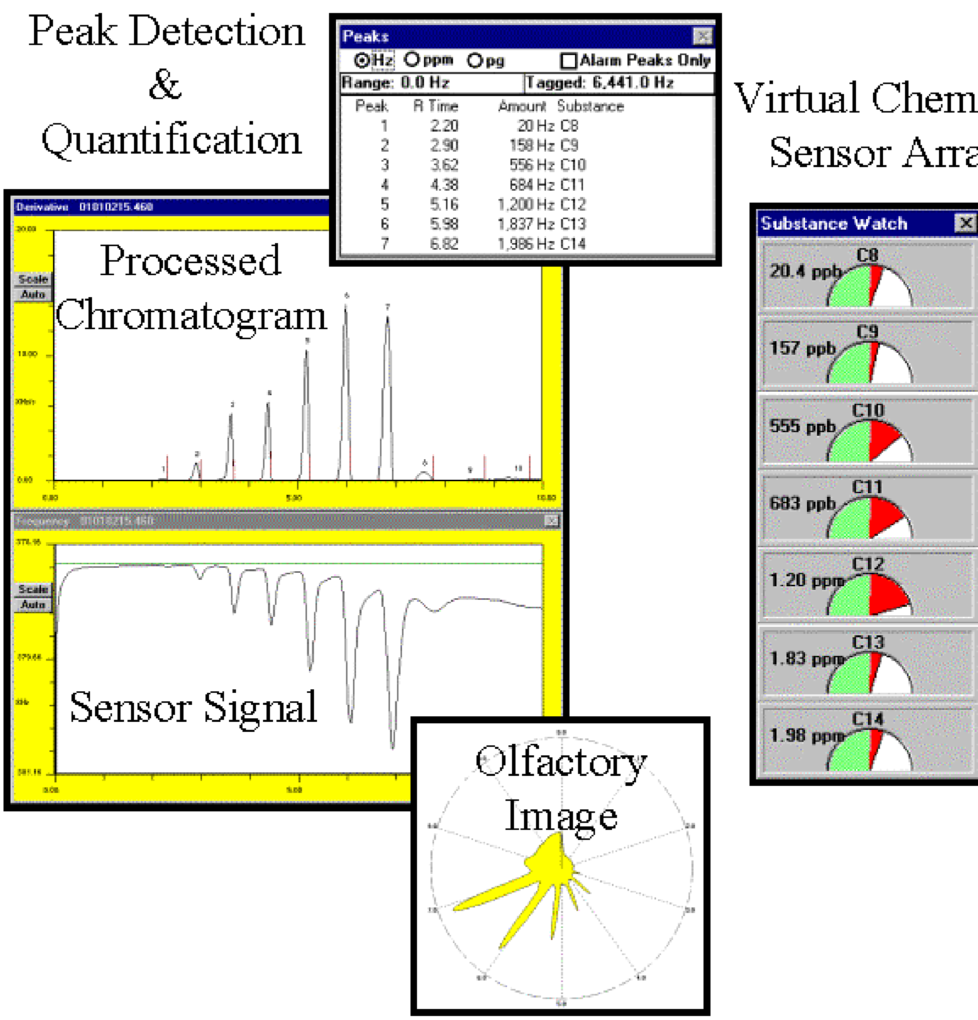


Figure 2- Features of zNose demonstrated using mixture of n-Alkanes on DB-624 Column.

Gasoline Headspace Measurements (DB-624)

Samples of gasoline with octane ratings of 87, 89, and 92 were obtained from a Thousand Oaks Phillips gas station. (Although Exxon had its corporate headquarters in Thousand Oaks at one time, a local Exxon Station could not be found).

The headspace vapors of a 250-mL bottle containing approximately 125 mL of gasoline at room temperature were sampled directly using a zNose™ equipped with a dB624 column. Gasoline is very volatile and known to contain a large number of hydrocarbons containing between 3 to 12 carbons. Because of the high concentrations of many of these vapors a detector setting of 60^{o}C and a 1-second sample time (0.5 mL) was used to test the headspace vapors of gasoline. The results of Figure 3 were obtained on 92-octane gasoline. It is notable that two low molecular weight compounds, heptane (peak 4) and iso-octane (peak 5)) are quite pronounced and dominate the headspace vapors of gasoline.

Also seen in Figure 4 is a tabulation of peaks with their retention time, and integrated signal level, as well as the Vaporprint™ olfactory image. The olfactory image is meant to provide an overall visual character to the smell of gasoline. There are approximately 10-12 higher molecular weight compounds which consititute the gasoline additives responsible for control of emissions and establishing the octane rating of the gasoline.

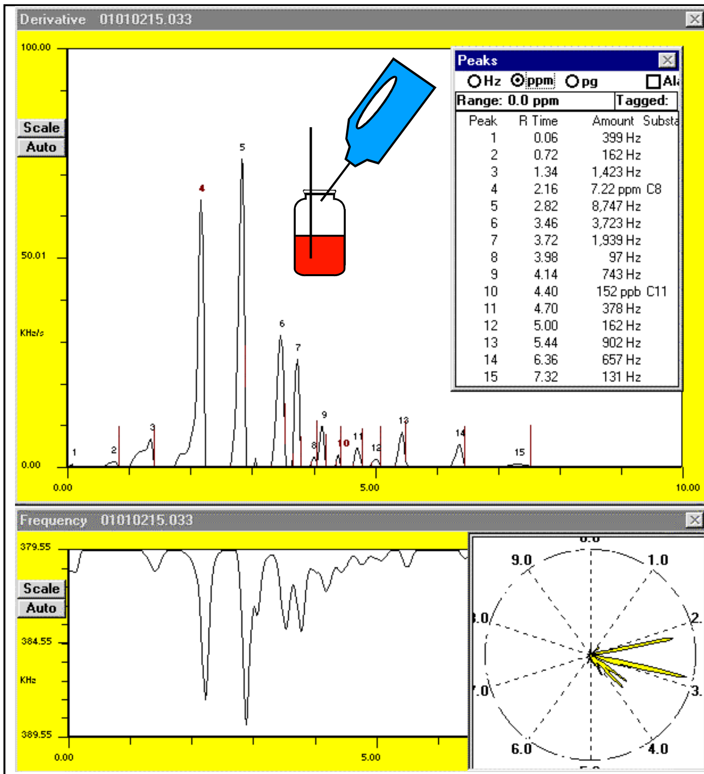


Figure 3- Analysis of Headspace vapors for 92-octane gasoline on a zNose with a dB-624 column. Heptane and iso-Octane (peaks 4 and 5) dominate the headspace vapors of gasoline.

Gasoline Vapor Measurements (DB-624)

Gasoline vapors were created by injecting 1 microliter of gasoline into a 40 milliliter vial fitted with a septa lid. The zNose was then able to sample the vapors directly with a standard side-ported sample needle. The results are shown in Figure 4. Because in this case the concentration of the compounds is not saturated, the distribution of high molecular peaks, the additives, are much more pronounced. The olfactory image is also much more diverse as well.

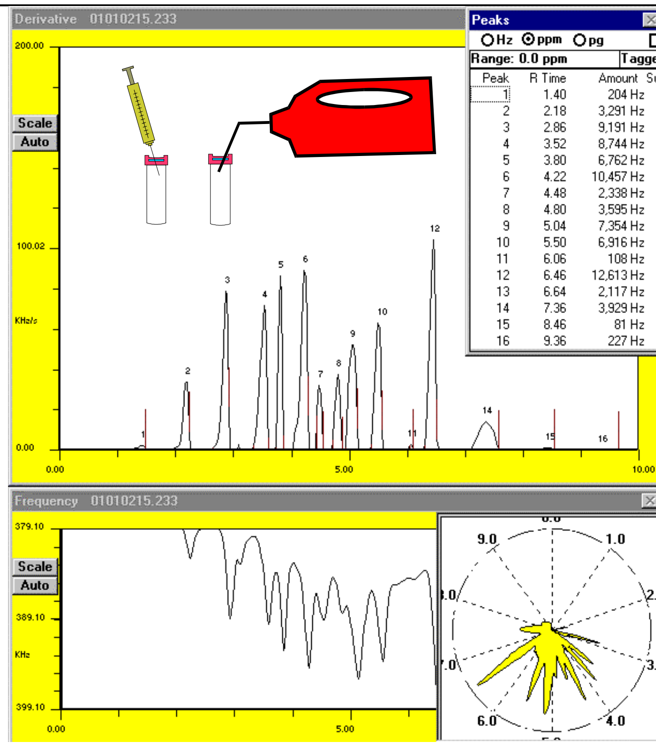


Figure 4- Testing of vapor standard created by injecting 1 µLiter gasoline into a 40 mL vial. A 10ps-2 method, 60° detector, and a 2.5 milliliter vapor sample was used.

Using offset traces, chromatograms of headspace vapor and unsaturated gasoline vapors are compared again in Figure 5. Headspace measurements are less susceptible to experimental errors due to injections but can suffer if not done at a controlled temperature. Unsaturated vapor measurements reveal more structure in the gasoline additives and are relatively insensitive to temperature.

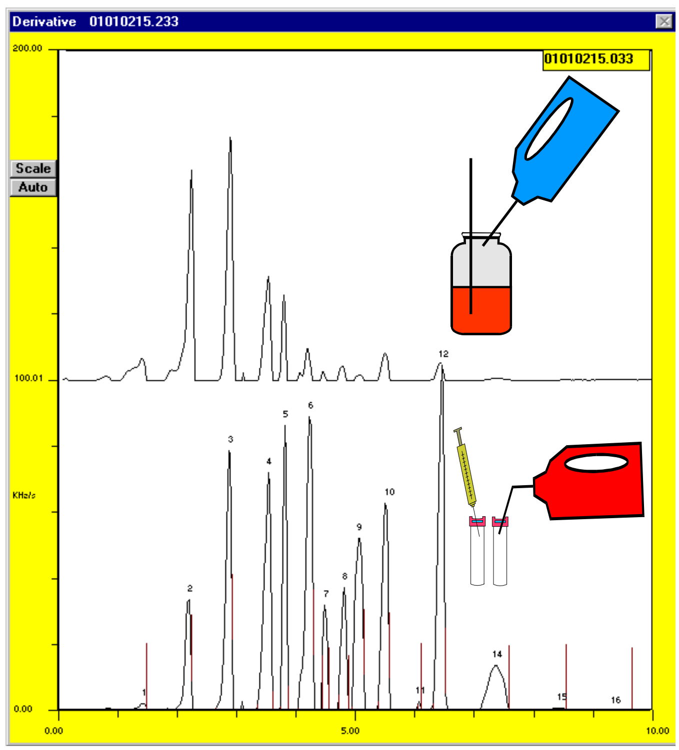
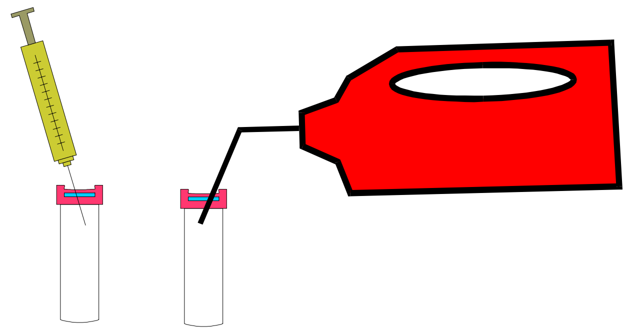


Figure 5- Comparison of Headspace analysis vs unsaturated vapor in vial.

Octane Comparisons (DB-624)

Each octane rated gasoline was tested as an unsaturated vapor by injecting 1 microliter into a 40 milliliter vial. Using offset chromatograms the results are shown in Figure 6. The additives are nearly identical for all compounds except the highest molecular weight and it is presumed that these are the compounds most responsible for achieving the desired octane rating.



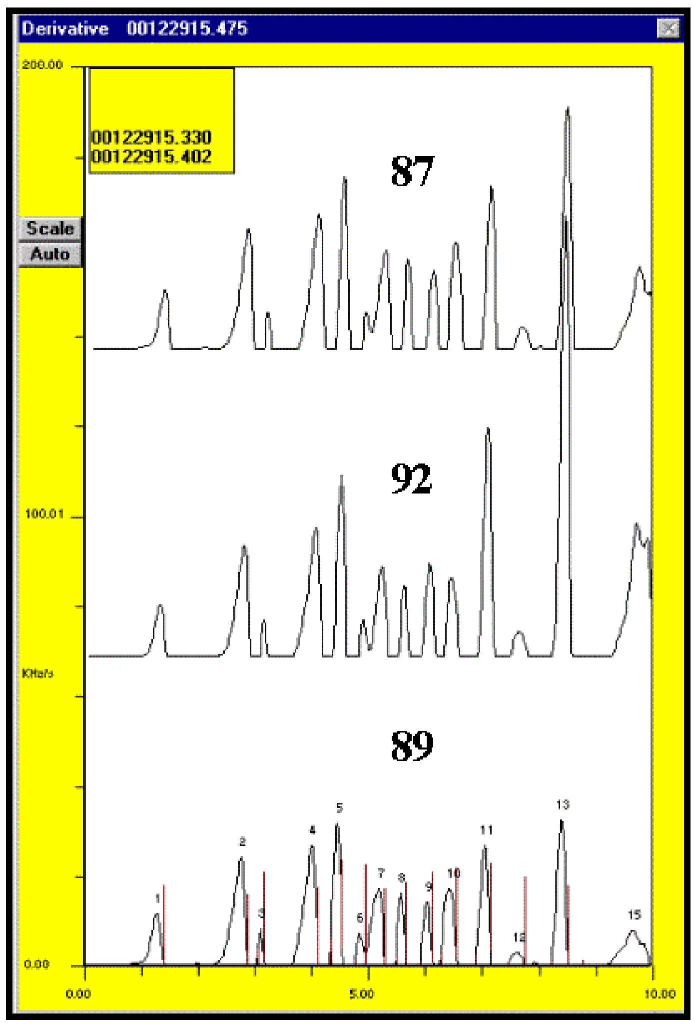


Figure 6- db624 comparison of gasoline of different octane ratings.

Measurements with a DB-5 Column

A zNose equipped with a dB-5 column is capable of much higher temperatures and hence is able to more easily resolve and analyze high molecular weight compounds up to approximately C30. Shown in figure 7 are offset traces showing the response obtained using mixtures of alkanes and different temperature ramp rates with the dB-5 column. Slowing the ramp down to 5°C/second (bottom trace) spreads out the analyte spectrum.

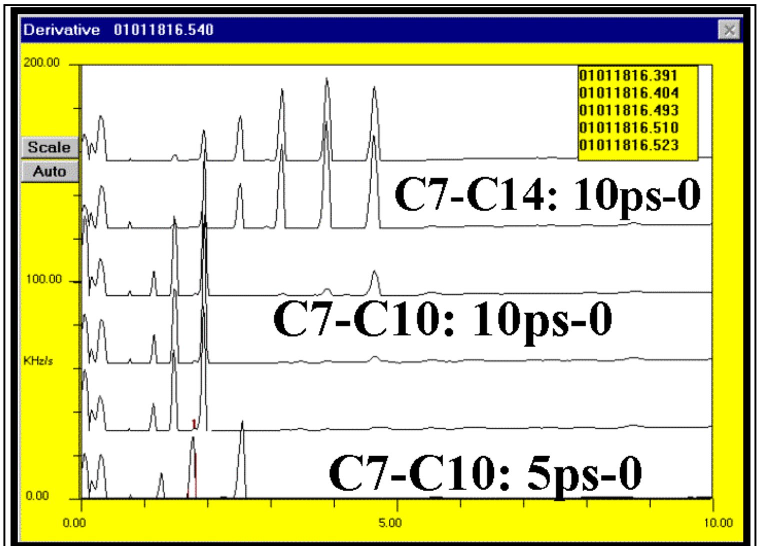


Figure 7- Alkanes on a db 5 equipped zNose with 10°C/sec and 5°C/sec column ramp rates.

Reducing the ramp rate to 2°C/second, shown in figure 8, achieves a spectrum more like the previous 10°C/second ramp on a DB-624 column. Here the spectrum covers C7 through C12 and was used in the testing of gasoline vapors.

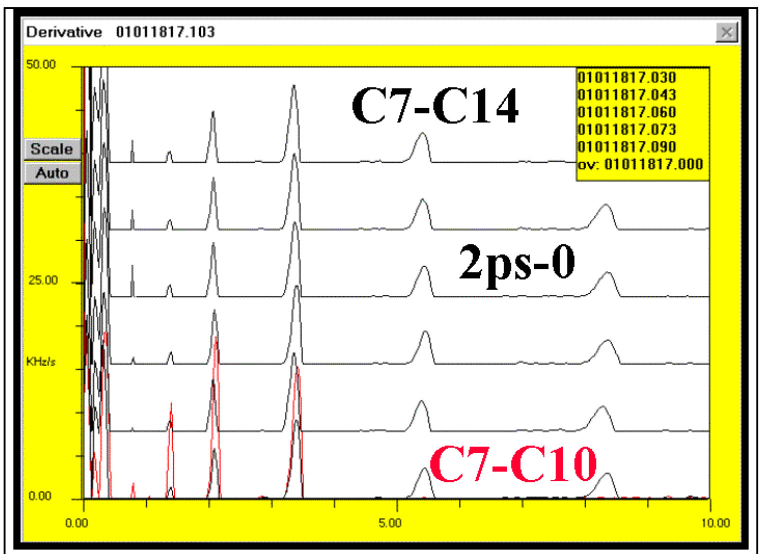


Figure 8- Alkanes with a slow temperature ramp of 2°C/second on dB5 column

Testing Headspace Vapors (DB-5)

Shown in Figure 9 is the headspace vapors analysis performed on 92 octane rated gasoline using a DB-5 Column. The DB-5 column was temperature programmed at 2^{o}C/sec from 40^{o}C to 60^{o}C and nominally gives better separation of the high molecular weight compounds.

Compared in RED are the alkane same analysis using a series of linear carbon chain alkanes. The heptane response is somewhat lower that previous analysis using DB-624 column, however, the iso-ocatane response remains high.

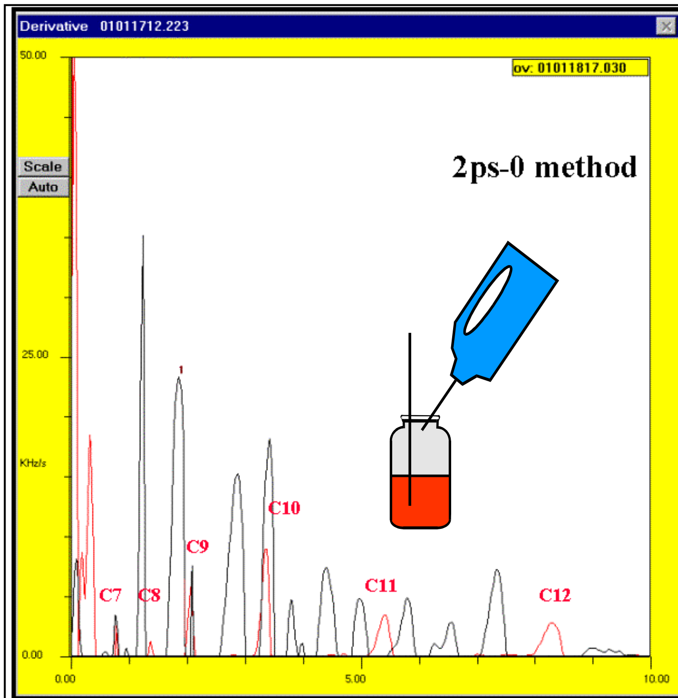


Figure 9- 92 Octane gasoline on DB 5 column and slow method

Comparison of Gasoline Headspace Vapors (DB-5)

Figure 10 shows comparison of headspace vapors overlaid so as to obtain comparisons for gasoline with octane ratings of 87 and 92. With the exception of one volatile peak near 0.95 second retention time, the two octane rated gasolines are nearly identical when viewed on this scale. In the lower trace the results have been expanded so as to better compare the concentration of gasoline additives. Here it is clear that only the higher molecular weight compounds are different.

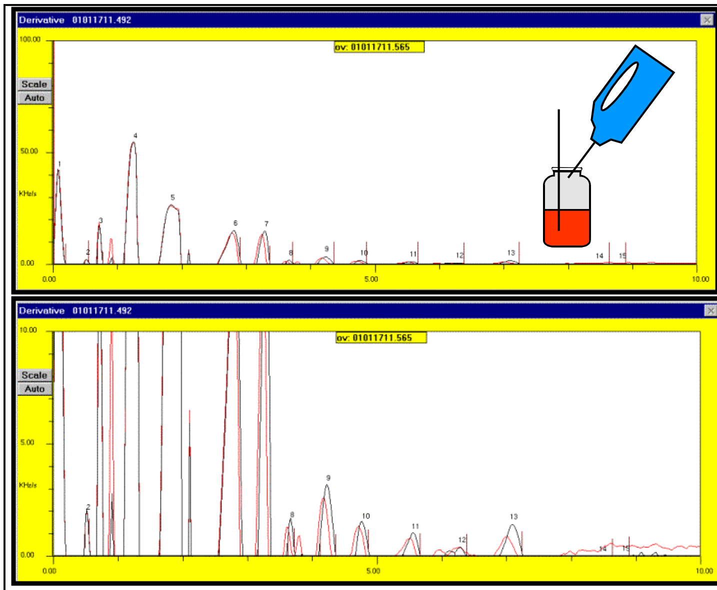


Figure 10- Headspace measurements with db5 on 87 and 92 octane gasoline. 87 octane gasoline is plotted in RED.

The zNose software can quantify the concentration of each analyte in Figure 9 using peak detection software. The results for the two grades of gasoline are shown in Figure 11. The major difference appears to be in the concentration of the peak 13 additive where 87 octane gasoline gives 172 Hz while 92 octane gasoline gives 284, or nearly double the concentration.

92 Octane

Peaks

OHz ⊙ppm Opg □Al

Range: 0.0 ppm Tagged:

Peak	R Time	Amount	Subs
1	0.08	3,209 Hz	
2	0.52	117 Hz	
3	0.72	907 Hz	
4	1.26	8,126 Hz	
5	1.84	6,479 Hz	
6	2.82	3,028 Hz	
7	3.30	1,864 Hz	
8	3.68	129 Hz	
9	4.24	503 Hz	
10	4.78	207 Hz	
11	5.58	161 Hz	
12	6.30	28 Hz	
13	7.10	284 Hz	
14	8.48	26 Hz	
15	8.84	23 Hz	
16	10.82	60 Hz	

87 Octane

Peaks

OHz ⊙ppm Opg □Al

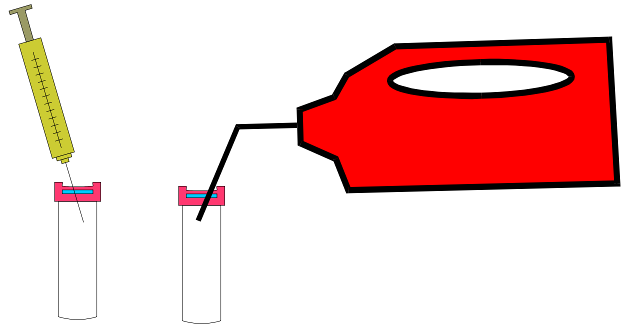
Range: 0.0 ppm Tagged:

Peak	R Time	Amount	Subs
1	0.08	3,442 Hz	
2	0.52	107 Hz	
3	0.72	962 Hz	
4	0.90	562 Hz	
5	1.26	8,353 Hz	
6	1.84	6,591 Hz	
7	2.80	2,663 Hz	
8	3.26	1,558 Hz	
9	3.64	105 Hz	
10	4.20	371 Hz	
11	4.72	192 Hz	
12	5.52	139 Hz	
13	5.98	29 Hz	
14	6.28	65 Hz	
15	7.02	172 Hz	
16	8.64	37 Hz	
17	9.32	42 Hz	
18	10.08	26 Hz	

Figure 11- Quantitative Headspace measurements on db5 system

Comparison of Gasoline Unsaturated Vapors (DB-5)

Performing an injection of 1 microliter of gasoline into an empty 40-milliliter vial and testing with the zNose provides improved signal levels for the gasoline additives. Gasoline with octane ratings of 87 and 92 are shown in Figure 12 using this technique. The comparison is done by vertically offset chromatograms as well as overlaid chromatograms with 87 octane plotted in RED. As before the primary difference between the two grades appears to be the high molecular weight additive with a retention time of approximately 7.3 seconds.



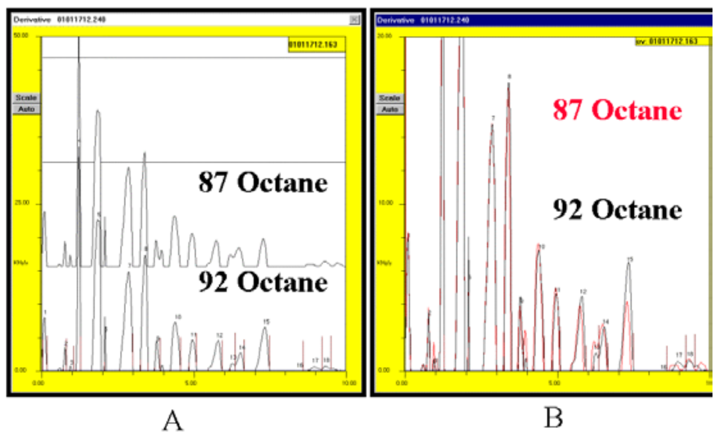


Figure 12- Comparison of low and high oxtane gasoline

Quantification of the above results is shown in Figure 13. In this case the 92 octane gasoline gave 1,649 Hz while the 87 octane gave a reading of 795 Hz. This additive seems to be approximately double in concentration for the 92-octane gasoline which is in agreement with the headspace findings..

92 Octane

Peaks

OHz ⊙ppm Opg

Range: 0.0 ppm Tagged:

Peak	R Time	Amount	Subs
1	0.08	399 Hz	
2	0.60	25 Hz	
3	0.76	207 Hz	
4	0.96	39 Hz	
5	1.22	2,537 Hz	
6	1.86	4,477 Hz	
7	2.08	88 Hz	
8	2.86	3,744 Hz	
9	3.40	2,787 Hz	
10	3.80	480 Hz	
11	4.40	1,598 Hz	
12	4.98	836 Hz	
13	5.82	1,004 Hz	
14	6.28	92 Hz	
15	6.56	385 Hz	
16	7.36	1,649 Hz	
17	8.48	62 Hz	
18	8.98	112 Hz	
19	9.34	73 Hz	
20	11.02	1,669 Hz	
21	11.82	38 Hz	

87 Octane

Peaks

OHz ⊙ppm Opg

Range: 0.0 ppm Tagged

Peak	R Time	Amount	Sub
1	0.08	395 Hz	
2	0.58	23 Hz	
3	0.76	192 Hz	
4	0.94	95 Hz	
5	1.22	2,690 Hz	
6	1.84	4,749 Hz	
7	2.86	3,701 Hz	
8	3.40	2,640 Hz	
9	3.78	345 Hz	
10	3.96	127 Hz	
11	4.38	1,680 Hz	
12	4.96	924 Hz	
13	5.76	835 Hz	
14	6.22	153 Hz	
15	6.50	405 Hz	
16	7.30	795 Hz	
17	8.34	31 Hz	
18	8.94	91 Hz	
19	9.34	157 Hz	
20	9.74	98 Hz	
21	10.86	1,115 Hz	

Figure 13- Quantitative results on db5 column

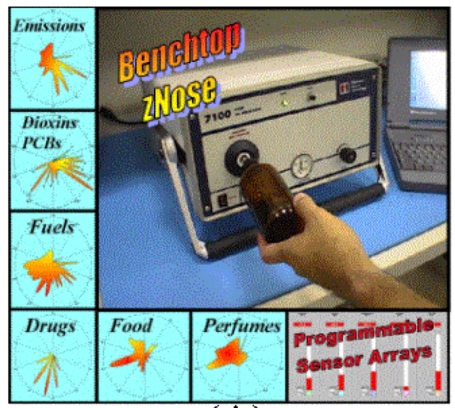
Summary

Final octane rating in gasoline is achieved through the addition of chemical additives to the basic heptane/iso-octane base. Flash chromatography provides a fast and accurate method of measuring the concentration of these additives. However, the octane rating of gasoline is currently arrived at by testing a special engine equipped with a knockameter. The zNose is able to measure the concentration of the additives using the headspace of the gasoline or by creating an unsaturated vapor by injection. The latter method gives higher signal levels than headspace testing.

Precision and accuracy in the zNose is excellent with RSDs typically in the 1-2% range when tested on constant BTEX vapor standards. However, the zNose measurement can be no more stable than the vapor concentrations which are presented to it. Obtaining a reliable and stable vapor source is not always easy.

The zNose is available in two configurations as shown in Figure 14. The benchtop system, our model 7100, is our most economically priced unit. With a state of the art Pentium laptop bundled with the latest Office suite, PC Anywhere, and many other useful software programs, it is priced at $19,450. If you prefer to purchase a model 7100 without a computer the price is is $14,950.

The model 4100, our handheld system, is ideal for those hard to reach situations where it is difficult to capture vapors or where it is desired to test vapors surrounding an object. The model 7100 price with computer is $24,950 and without a computer it is $20,450. We would be only too happy to submit a quotation.



(A)

(B)

Figure 14- zNose™ commercial instruments come as benchtop (A) or handheld (B) instruments. Both versions are fully portable and contain their own helium gas supply.