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Diagnosis of used engine oil based on gas phase analysis

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A method for determination of the volatile compounds present in new and used petroleum oils was developed. The identification of the new and used oils was based on the abundance of volatile compounds in headspace above the oils. Multivariate analysis based on principal component analysis (PCA), and hierarchal cluster analysis was used to evaluate the degradation compounds found in used engine oil. The gas phase of new and used petroleum oils was analyzed using a time of flight mass spectrometer (TOF MS) and sensor arrays. The samples included used engine oil, up to 35,500 miles. The principal components identified by PCA were volatile constituents of the oils. New and used oils were also differentiated using multivariate analysis of the results from these gas phase detection methods. The identification of the origin of volatile samples in the used oils has been studied by spiking newer oil samples with a complex mixture of volatile compounds. These samples were then analyzed with the sensor array. Results from the spiked samples correlated better with the older, more used oil samples, confirming that the previously identified volatile compounds can be used to classify new and used engine oils. Using chemometrics, the used oils were differentiated into categories using metal oxide semiconductor (MOS) and quartz crystal microbalance (QCM) sensor arrays or mass spectrometry. The QCM sensors were able to better differentiate the new and used oil samples compared to the metal oxides. In the mass spectrometry and sensor array analysis the new oils were clustered into groups and separated by mileages. The older, more used oils were clearly distinguished from the newer oils.

Introduction

Many studies have used the electronic nose technology to provide quality control information in commercial manufacturing.[1] Although the resulting information is not quantitative, it provides directional information about the change in the stability over time of the studied material and can discriminate between samples of relatively minor differences. Developments of *in situ* electrochemical oil-condition sensors have been reported[2,3] but the measurements were done in liquid phase.

The influence on the sampling temperatures and the abundance of volatile compounds has been studied.[4,5] The overall abundance of volatile compounds increases with the increased temperature of the sampling prior to detection. This is due to the vapor pressure increase with temperature, therefore increasing the presence of volatile compounds present in the sample headspace.

Our goal is to develop an on-board sensor to diagnose used oil in an automobile.

In a previous report,[6] used engine oils were analyzed by GC MS and found that 'blow by' components and therefore overall abundance of volatile compounds increased over use of the oils. Primarily, these volatile compounds were substituted benzenes. The process by which unburned gasoline is absorbed into the engine oil is well known.[7,8] It enters into the oil through oil film on the cylinder wall and oil in the ring grooves. It is vaporized from the oil in the crankcase. Quantification of gasoline fraction of crude oils and structure group analysis, or 'finger printing' has been done using high resolution capillary gas chromatography.[9,10] As expected, the resulting compounds identified are primarily volatile compounds.

Experimental

Oil samples

The most common engine lubricant oil 10W-30 viscosity grade for automobile engines (Pennzoil brand) was used. Used oil samples were collected from a passenger car (gasoline powered, 1996 Toyota Tercel, about 90,000 miles), which had consistently used Pennzoil 10W-30 as its engine lubricant. The oils were removed from the car at 235, 4080, and 8376 miles. Additionally, engine lubricant oil was collected at mileages of 628, 1273, and 1945 miles from a 2003 Jeep Grand Cherokee. Used oil samples were provided by Savant, Inc with 550, 1375, 2200, 3003, 3025, 3850, 4675, 6000, 15000, 17250, 26500, and 35500 miles that had been collected from a test engine. Also included was a new oil sample of 5W-30 (Pennzoil brand) as a reference point. Spiking experiments were done with new and 235 miles oils with the Aromatics Mix from Sigma Aldrich.[11]

Headspace analysis by GC MS using solid phase microextraction (SPME) and time of flight mass spectrometry (TOF MS)

A LECO Pegasus III Time of Flight Mass Spectrometer (TOF MS) equipped with a Gerstel Multi Purpose Sampler MPS2 was used in this study. Approximately 50 mg of oil sample was weighed into a 20 mL glass vial and incubated for 2 min at 140 °C at an agitation speed of 500 rpm for 60 s. Next, the oil sample vial was pierced and the headspace of the oil was exposed to a Stable Flex Divinylbenzene/Carboxen/Polydimethyl siloxane (PDMS), for the SPME. The stationary phase was 50 μm with a film thickness of 30 μm (Supelco part number 57328-U). The GC column was a HP-5MS, Hewlett Packard part number 19091S-413 with a film thickness of

20 m × 180 μm × 0.18 μm and coated with 5%-phenyl methylpolysiloxane cross linked. The initial GC oven temperature was 50 °C for 1 min and increased at 17.5 °C min^{-1} to 275 °C and held there for 5 min. The gas phase injection was made splitless and the flow rate was constant at 0.8 mL min^{-1}. The mass spectrometer was operated in electron ionization mode collecting in a mass range of 35–450 atomic mass units at an acquisition rate of 40 spectra s^{-1}. Identification of unknowns in the samples was carried out by comparison of their spectra with the NIST/EPA/NIH spectra library #359-001-200. The criteria selected in the initial library search were based on a similarity index greater than 700. This index is labeled as "Q". The spectra were then manually reviewed for validity.

Gas phase analysis using the ALPHA MOS

The ALPHA MOS model FOX 4000 was made up of metal oxide semiconductor (MOS) and quartz crystal microbalance (QCM) sensors. A total of 24 sensors were used in the array. A description of the sensors is given in the FOX 4000 manual.[12]

A DANI HSS 86.50 headspace autosampler was used to inject samples of oil into the Fox 4000 model. The oil samples (50 mg) were heated at 140 °C for 5 min in 20 mL sealed glass vials. The headspace of the oil was sampled by the DANI HSS 86.50 using a splitless mode transfer line at 160 °C directly into the Fox system. The Fox system acquisition time was 120 s and a flow rate of 300 mL min^{-1} of air. A delay of 780 s for purging was used between each acquisition to allow time for the sensor to recover.

The detection principle of the MOS sensor is based on the change in the resistance of the metal oxide when in contact with the analyses. The QCM detection principle is based on the change of the resonance frequency of the quartz crystal due to the analyte absorbing by the sensor coating.

A single data point at a specific point in time was used for each sensor response to a sample. For the MOS sensors, the point chosen per sensor was the maximum percentage change in resistance of the sensor during the acquisition period for each samples, $\partial R_{max}/R_0$, where ∂R_{max} is the maximum response of sensor and R_0 is the initial baseline resistance of sensor. The QCM sensor data was normalized to convert the change in frequency response to change in resistance so that the output of the data could be evaluated graphically from one graph. This type of evaluation was set by the FOX 4000 system. The results were analyzed using a PCA which was included in the software package. After injection, the sample was passed for the first 60 s through chamber one with the four QCM and then through the chambers two, three and four with MOS sensors. The total acquisition time was 120 s.

Principal component analysis (PCA) for GC MS data

The abundance of volatile compounds was compared to the mileage of the oil samples. PCA was used to estimate which compounds should be grouped together to explain the variability in the data. To perform the PCA, the 'factor analysis' was chosen in the SPSS version 10 Base software (http://www.spss.com).[13] The extraction method of principal components was specified and used to analyze the correlation matrix.

We evaluated which grouping of compounds (principal component) best differentiated the oil samples into age groups, and which had principal component scores that best correlated with the mileage abuse level (increased component score as the mileage increased) for each oil sample. After identifying a principal component that met these criteria, we evaluated the component loading scores of those compounds to determine which were most important. From this subset, the signature compounds were selected.

Principal component analysis (PCA) for the Alpha MOS Fox 4000

The PCA constructs linear combinations of the original data with maximal variance. This reduces the number of variables represented by the 24 sensors responses and the associated time, to a smaller number of components with minimal loss of information. The method involves eigen value and eigen vector extraction from a variance–covariance or correlation matrix. The eigen values give the amount of variance accounted for by each principal component. The eigenvectors are coefficients in linear transforms of the original variables. The method extracts as many components as necessary to account for the linear structure in the original variables. The first component is represented by the x-axis and accounted for the greatest portion of the variance. The second component is represented on the y-axis and accounted for the second largest contribution of the variance. For the Alpha MOS data analysis, we used a 'non-reduced' method that uses raw values for calculating the variance. Another option was to use the 'reduced' method where each variable (sensor output) is normalized and column of the data matrix is divided by its standard deviation. Our data was best described using the non-reduced method and is reported as such in every case.

Cluster analysis

The basic concepts of cluster analysis are *similarity and distance*. Distance measures how far apart two objects are while similarity measures closeness. "Ward's method" was chosen for our cluster analysis. It is distinct from all other methods because it uses analysis of variance approach to evaluate the distances between clusters. In short, this method attempts to minimize the sum of squares (SS) of any two (hypothetical) clusters that can be formed at each step. In general, this method is regarded as very efficient; however, it tends to create clusters of small size.[14] Specifically, SPSS version 11 Base software was used for the analysis.[13] The former PCA resulted in regression factor scores for each used oil sample. These scores were input as variables for the Ward cluster analysis. The resulting dendograms were then analyzed to determine similarity. Using the Euclidean distances, the vectors are compared. Within each subset the samples that are most closely linked to the origin (the left most point) are the most similar and have the most closely situated vectors.

Results and discussion

GC MS TOF analyses

The oil samples were analyzed by SPME and detected with GC MS TOF. The results of the total volatiles were summed for each oil sample and plotted in Fig. 1. The new oil had the
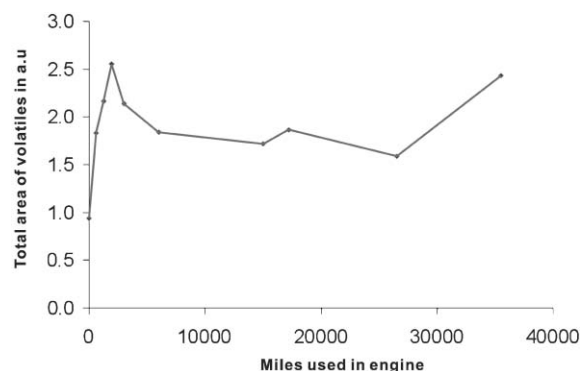
Fig. 1 Total area of volatiles from SPME headspace of used oils detected by GC TOF MS *vs.* miles used in engine. Note that steady state of volatiles is reached approximately after 6000 miles.

Table 1 Top 30 compounds identified by GC TOF MS in oil samples up to 35,500 miles in decreasing amount of abundance

1,2,4,5-Tetramethylbenzene	5*
1-Methyl-4-(1-methylpropyl)benzene	6*
1-Propenyl-(E)-benzene	3*
4-Ethyl-1,2-dimethylbenzene	4*
Propylbenzene	2*
Ethylbenzene	1*
Hexadecane	7*
Nonadecane	8*
1,3,5-Cycloheptatriene	
2,3-Dihydro-5-methyl-1H-indene	
(1,1-Dimethylpropyl)benzene	
(1-Methylethyl)benzene	
1,2,3,4-Tetramethylbenzene	
1,2,3-Trimethylbenzene	
1,2,4-trimethylbenzene	
1,2-Diethylbenzene	
1,2-Dimethylbenzene	
1-Butenyl-(E)-benzene	
1-Ethyl-2-methylbenzene	
1-Methyl-2-(1-methylethyl)benzene	
2-Ethenyl-1,3,5-trimethylbenzene	
2-Ethyl-1,4-dimethylbenzene	
Benzo[b]thiophene	
Biphenyl	
Cyclopenta[b]thiapyran	
Dibutyl phthalate	
Dodecane	
Heptadecane	
1,4,5-Trimethylnaphthalene	
2,6-Dimethylnaphthalene	
n-Pentadecylcyclohexane	
3-Methyloctadecane	
Phenol	
Undecane	

[a] PCA was done to classify the compounds as signatures (*) due to their loading of ± 0.7 in PC 1 and 2. Compounds are numbered in the GC TOF chromatogram, Fig. 2.

lowest abundance of volatile compounds. The abundance of volatile compounds increased in samples up to 1945 miles used sample; after that a steady state was reached for samples from approximately 6000 up to 35,500 miles.

The overall total volatiles are comprised of substituted benzene compounds as listed in Table 1. They are formed during oil usage in the engine at steady state. Fig. 2 shows the
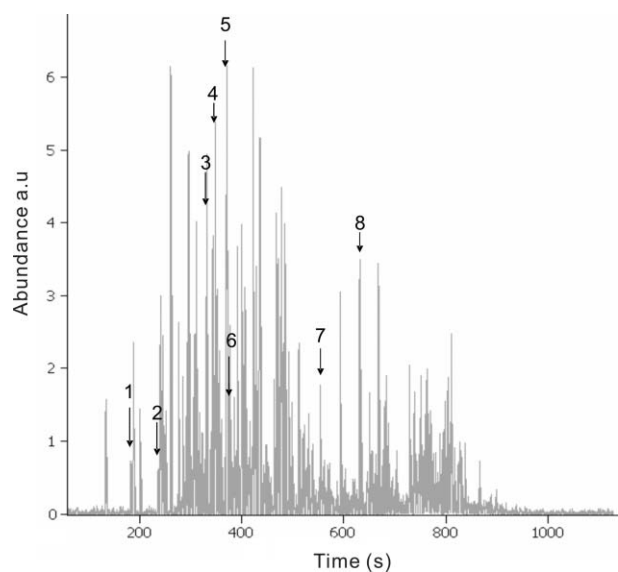
Fig. 2 Total ion chromatogram using TOF from a headspace injection of a SPME of 6000 miles used oil sample. Signature compounds are identified in Table 1.
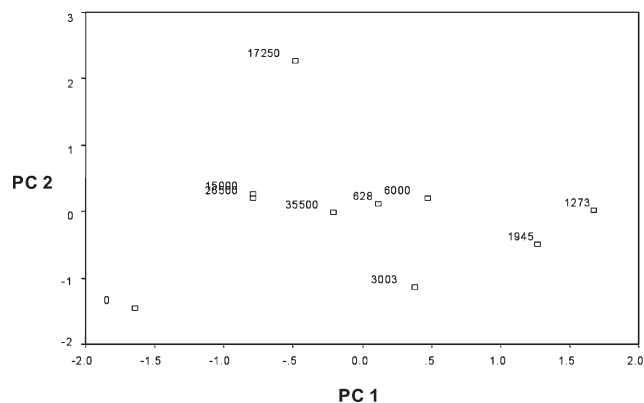
Fig. 3 Principle component analysis of used oil samples. The data for the PCA was collected from GC MS TOF of a SPME headspace of the oils. Input data included the area and compounds identified from all samples of the 30 most abundant volatile compounds.

GC TOF MS analysis of a 6000 miles used oil sample and compounds that were determined to be signatures of used oils by the criteria selected which is explained below and identified in Table 1.

The top 30 most abundant volatile compounds detected from GC TOF MS of the SPME from all samples are listed in Table 1. Since the abundance of volatile compounds increased with increased mileage, we chose the area (abundance) of the top 30 compounds to be used in a principal component analysis to determine which compounds differed the most between the oil samples. This approach is commonly used to differentiate samples by factors which best describe the model of the data set.[15–17] Fig. 3 shows the principal component 1 and 2. PC 1 and PC 2 accounted for 43% of the variability. Compounds that scored ± 0.7 on these two principal components are represented by asterisks in Table 1. A hierarchical cluster analysis was done using Ward's method and a dendrogram produced by this technique is shown in Fig. 4. This technique was able to cluster the oil samples into two primary groups with the 6000 mile sample separating the 10 oils by mileages. On the left of the plot, each sample represents a class by itself. As the distance criteria is relaxed from 0 to 25, or as we move in the right direction on the plot, samples are clustered or grouped based on their mileages. As the distance is increased and the criterion of uniqueness is relaxed, more samples are included in the same cluster. This separation is also seen in the PCA in Fig. 3 if an imaginary line is drawn from the origin of the data and divides PC1 and PC2. This would indicate the 6000 mile interval is the point at which the used oil sample is clearly differentiated from the other samples by their volatile constituents. The steady state of the volatile compounds in Fig. 1 is reached at the 6000 miles interval of the used sample.
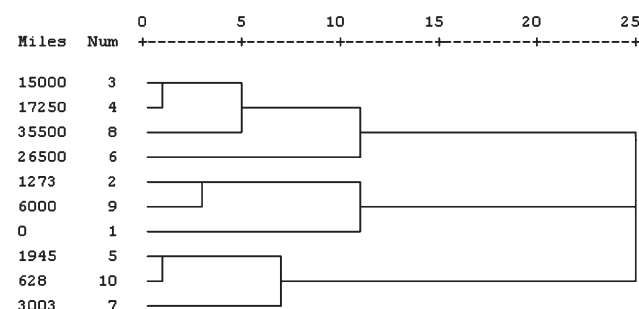
Fig. 4 Hierarchical cluster analysis and resulting sendrogram using Ward's method. This technique was able to cluster the oil samples into two primary groups with the 6000 mile sample separating the 10 oils by mileages.
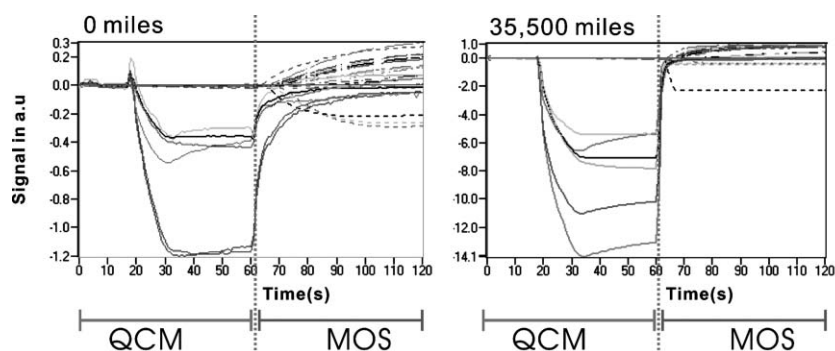
Fig. 5 Raw data output from the Alpha MOS sensing the headspace of the new oil and the oil used to 35,500 miles. The sample passes first through the QCM chamber (the first 60 s) and then through the MOS chambers for the remainder of the 120 s.

Alpha MOS Fox 4000 analyses

We next used an electronic nose (the Alpha MOS Fox 4000) to sense the vapor phase above oils using an electronic nose. The samples were heated to 140 °C, the same temperature used in the mass spectrometer analysis, and the approximate operating temperature of an automobile engine. The output of these 24 sensors for new and used oils (up to 35,500 miles used) is shown in Fig. 5.

In the first analysis, the four Pennzoil oils were measured using all 24 sensors in the array. The four oil samples consisted of unused oil, and three oil samples used for 235, 4080, and 8138 miles in an automobile. By sampling each oil sample thirty times, the sensors were able to differentiate between the four oils, and order them by increasing mileage. As shown in Fig. 6, we were able to form three groups by the PCA. The new oil and the 8138 miles used oils were grouped into two separate groups.

However, the 235 and 4080 miles used samples were clustered into one group, indicating that these two oils were essentially identical in overall volatile content. In order to correlate with our previous GC MS analysis which related the used oils to their overall increase in abundance of substituted benzene compounds, we spiked the new and 235 miles used samples with an 'aromatics mix' purchased from Supelco. Table 2 lists the compounds and their percent composition in the Sigma Aldrich mixture. Several of these compounds were defined as 'signatures' that describe the differentiation between new and used oils in our previous study. The new oil was spiked with 1, 2, 5, 7.5, 10, 20, and 30 µL of the 'aromatic mix' per 5 g oil sample. Additionally, the 235 miles sample was spiked with 1 and 2 µL of the 'aromatic mix' into the 5 g sample of the oils. As shown in Fig. 7, the sensor array was capable of differentiating the spiked samples with the 'aromatic mix' from the un-spiked samples. The spiked samples clustered more closely with the more used samples, as did the samples with increasing amounts

Table 2 Aromatic mix used in spiking experiments (Sigma Aldrich product #44587)

|	
1,2,4,5-Tetramethylbenzene	1.97%
1,2,4-Triethylbenzene	3.10%
1,2-Diethylbenzene	3.06%
1,2-Dimethyl-3-ethylbenzene	2.96%
1,2-Dimethyl-4-ethylbenzene	2.71%
1,3,5-Trimethylbenzene	3.43%
1,3-Dimethyl-2-ethylbenzene	2.70%
1,3-Dimethyl-5-ethylbenzene	1.31%
1,4-Dimethyl-2-ethylbenzene	2.99%
1-Methyl-2-ethylbenzene	4.46%
1-Methyl-2-isopropylbenzene	2.63%
1-Methyl-2-n-propylbenzene	1.45%
1-Methyl-3-ethylbenzene	2.90%
1-Methyl-3-isopropylbenzene	1.40%
1-Methyl-3-n-propylbenzene	3.21%
1-Methyl-4-ethylbenzene	3.17%
1-Methyl-4-isopropylbenzene	2.79%
1-Methyl-4-n-propylbenzene	1.44%
2-Methylbutylbenzene	1.43%
Benzene	3.14%
Ethylbenzene	1.57%
Isobutylbenzene	0.85%
Isopropylbenzene	3.13%
Toluene	4.56%
m-Xylene	2.94%
n-Butylbenzene	2.89%
n-Hexylbenzene	4.64%
n-Pentylbenzene	1.47%
n-Propylbenzene	1.71%
o-Xylene	3.21%
p-Xylene	2.98%
sec-Butylbenzene	1.47%
t-1-Butyl,3,5-dimethylbenzene	2.92%
t-1-Butyl-4-ethylbenzene	2.90%
tert-Butylbenzene	2.67%
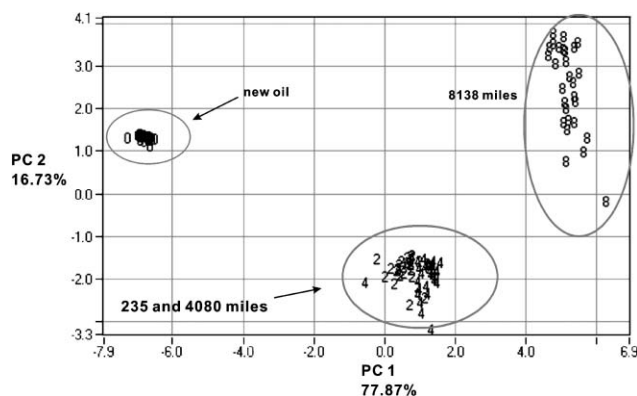
Fig. 6 PCA of Alpha MOS results of new oil and 235, 4080, and 8138 miles used oil samples.
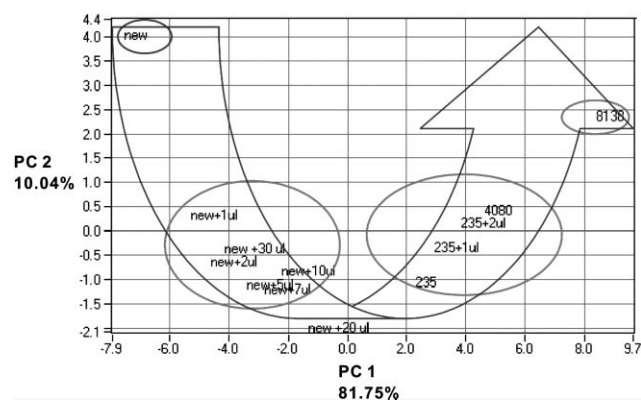
Fig. 7 PCA of Alpha MOS results of oil samples (new and 235 miles) spiked with an aromatic mix.[11] The overall volatile compounds increases with the PC1 on the positive scale.
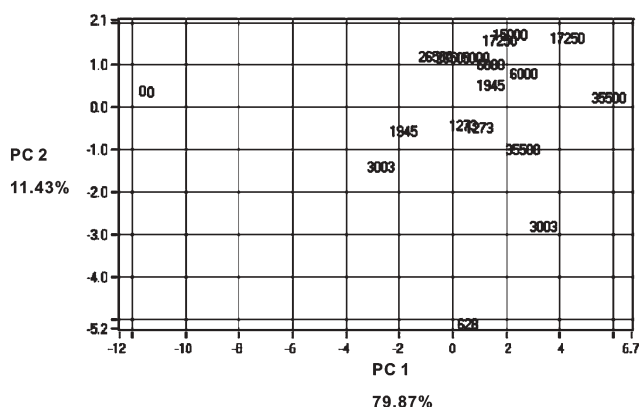
Fig. 8 PCA of oil samples analyzed with Fox 4000 using both MOS and QCM. Samples noted by miles used were run in duplicate (except the 628 miles used sample).

of the spiked mixture. This correlates well with our analysis by GC MS, suggesting that these benzene substituted compounds are responsible for the volatile 'signature' of the used oil samples *vs.* the new, unused oil.

Four basic groups were classified in Fig. 7:

1. the new (unused) oil,

2. the new oil spiked with 1, 2, 5, 10, 20, and 30 μL of the aromatics mix,

3. the 235 miles sample, the same sample but spiked with 1, 2 μL of the aromatic mix and the 4080 miles samples,

4. the 8138 miles sample.

This data correlates with that of Fig. 6, where the 235 and the 4080 miles used samples were grouped together. However, when the 235 miles used sample was spiked with increasing amounts of the aromatic mix, the relationship was further increased, thereby decreasing the distance between the samples. In both Figs. 6 and 7 the overall abundance of volatile compounds increased with the PC 1 on the positive scale.

Fig. 8 shows the PCA from the collected data using both QCM and MO sensors demonstrating that two principal components accounted for more than 92% of the variability. The PCA correlated the increasing abundance of volatile compounds with both PC1 and PC2 on the positive scale of the Eigen values. In other words, the 0 miles used sample had the least amount of volatile components, whereas the 17,250 and 35,500 miles used samples had the most volatile compounds present. This indicates that the electronic nose is reliable and can differentiate samples by their volatile constituents.

The data was analyzed using only the QCM sensors to determine if they were more efficient in differentiating between the samples, Fig. 9. A PCA was done with the collected data; two principal components accounted for more than 99.5% of
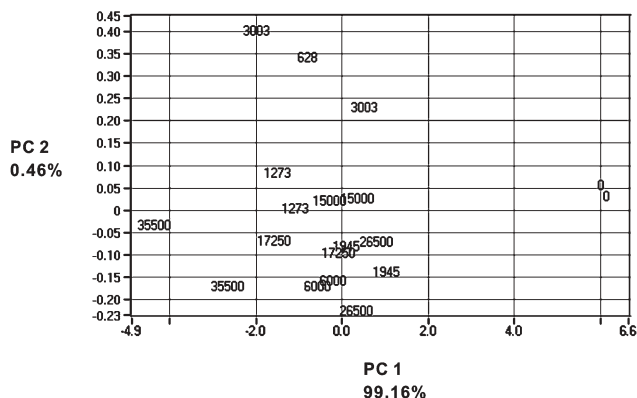
Fig. 9 PCA of oil samples analyzed with Fox 4000 using QCM only (no MO). Samples noted by miles were run in duplicate.

the variability. This indicates that more variance in the responses to the used oil vapors can be accounted for with the six QCM sensors alone than in the previous analysis that used both QCM and MOS sensors.

The PCA correlated the increased abundance of volatile compounds found in our previous analyses, relating both PC1 and PC2, this time on the negative scale of the eigen values. The MOS sensors did not provide as much useful information when compared to the QCM, and therefore diminished the discrimination power of the array. The QCM alone provided the best information. There can be a diminishing return from an increase in number of sensors in the array if these additional sensors are not adding valuable information.[18,19] The effectiveness of a chemical sensor array system is dependant on the availability of a diverse set of chemically independent materials and objective selections of the best film set for a particular problem.[20] The signatures we identified were less diverse than one might wish given that most of them are substituted aromatics and hydrocarbons. However, this makes the selection of the best film set even more important. The QCM outperformed the MO, and for this analysis was the only sensor necessary to provide the most accurate information. The patterns were acquired on the same samples, over period of one month without any noticable change.

Summary

The degradation of engine oil is a complex process. In addition to the known oxidation processes, the engine oil is subjected to 'blow by' from gasoline in the combustion process. This 'blow by' primarily consists of alkyl benzenes. As the oil is used, more of these compounds are accumulated.

Using mass spectrometry, hundreds of volatile compounds were identified in new and used oils. The most abundant volatile compounds were subjected to multivariate statistical techniques, including PCA and cluster analysis, to correlate these compounds with miles used in the engine. The top 30 volatile compounds were determined and the signature compounds responsible for the overall model of new *vs.* used oils. Gas phase signatures compounds, mostly alkyl substituted benzenes, were defined. The existing diagnostic procedures for oil degradation rely on analysis of the oil phase.[2,3,21,22] It would seem logical to use the presence of antioxidant additives as the "indicator". However, it has been noted before[6,23,24] that antioxidants become depleted from the oil very early, typically, below 4000 miles.

The electronic nose sensor array was able to correlate and differentiate the used oils by their increased mileages. The addition of the aromatic mixture and benzene to the newer oils resulted in the sensor correlating these spiked oils with older, more used oils. Overall, the primary differences between the used oils and the newer oils were the increased abundance of volatile oil-soluble compounds. Temperature proved to be a critical factor in the analysis of oil by either the sensor or GC MS. The analyses at higher temperatures were more successful at identifying the more used oils based on chemical composition rather than miles used in the engine. This indicates that the temperature used for sensing the oil will play a critical role in the sensitivity of that sensor. Our future work is aimed at designing a sensor array for the detection of the chemical composition of used oil that could be employed to determine optimal the time to change engine oil. The QCM sensors were found to be more efficient than the MOS sensors. The addition of the MOS did not provide useful information in differentiating the new oil from the used oils.

The chemometrics applied to the data was useful in reducing or eliminating non-discriminating information. Using PCA, thousands of identified compounds were eliminated, leaving

the most important compounds that could differentiate between new and used oil. These compounds were considered a signature of the used, or 'bad' oil. By cluster analysis, the used oil samples were grouped by the overall abundance of volatile compounds, which was also a direct correlation to mileage used on the oil. The utility of any diagnostic procedure depends on the stability of the baseline of the sensing array. In our case this difficult requirement would be somewhat mitigated by automatically re-setting the 'baseline' information after each intermittent test run.[25]

Acknowledgements

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