
A New Approach to the Noack Volatility Test

T. W. Selby Savant, Inc., Midland, Michigan, USA
E. A. Reichenbach Savant Laboratories, Midland, Michigan, USA
R. H. Hall Savant Associate, Midland, Michigan, USA

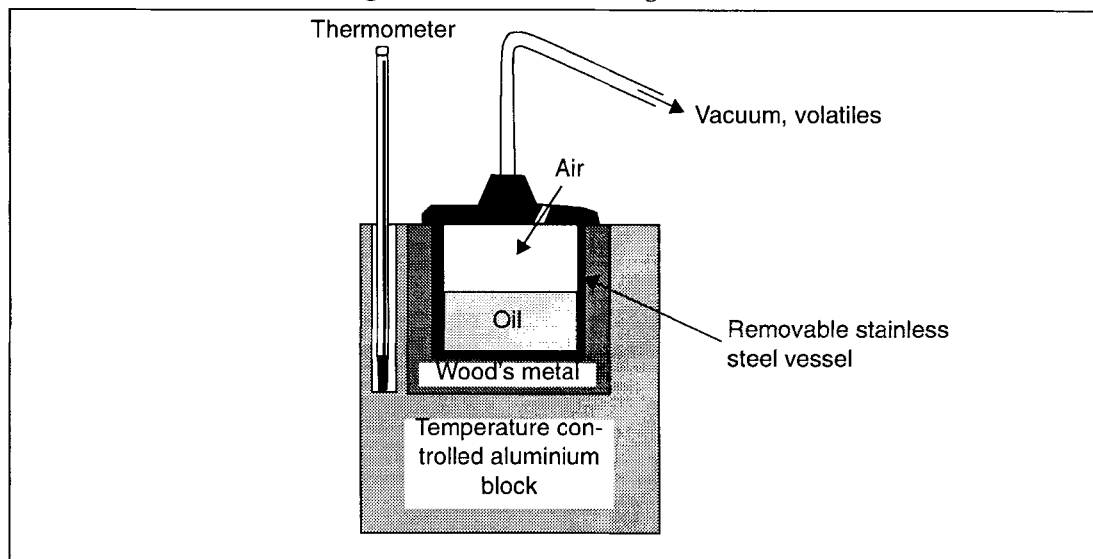
Abstract *This paper reports on the method and preliminary results of a significant modification of the Noack volatility test. This modification permits collection and examination of the volatile products as well as of the residue. The analysis of such volatiles by chromatography and spectroscopy revealed surprising information that is especially relevant in the face of increasingly difficult automotive and heavy duty engine emission limitations. The data also showed very close agreement with the Unified Test Method for the Noack Volatility Test now covered by CEC L-40-T-87. Important to operators, the authors' modified Noack apparatus avoids the use of the toxic Wood's Metal of the earlier Noack apparatus.*

Keywords *Noack volatility, modified Noack, residue, analysis, gas chromatography, spectroscopy, metals, ZDDP*

INTRODUCTION Volatility of an engine oil becomes important whenever the oil comes in contact with one of the high temperature zones in the engine, such as the turbo-charger, cylinder walls, valves, and the under-crown and ring-belt area of the pistons. An oil which has a high volatility not only increases the volume of oil consumed by the engine but the loss can also change the oil's effectiveness as a lubricant. Further, and of increasing importance, such volatile material can poison a catalytic converter, used to control emissions, over an extensive period of use.

Since control of engine oil volatility is so important to the function and use of the vehicle, methods of bench testing this property have been developed and used. Today there are tests, such as Simulated Distillation by gas chromatography (ASTM D 2887) and Noack volatility CEC L-40-T-87.

Figure 1 Noack's volatilising chamber



The Noack Volatility Test

The latter test came about as a result of some interesting volatility work done by K. Noack and reported in 1936.¹ A simplistic schematic of the volatilisation chamber, the heart of Noack's device, is shown in **Figure 1**. Evenly distributed heating of the sample held in a stainless steel vessel was accomplished through contact with molten Wood's Metal as shown in the sketch.

Noack's work led to the DIN 51.581 test technique² which, while useful and repeatable in determining engine oil volatility within a given laboratory, was considered to have relatively poor reproducibility.

Unified Test Method

When a maximum allowable volatility level for engine lubricants was considered desirable for vehicles in Europe, a Unified Test Method Committee was formed to re-evaluate and improve Noack's original procedure. The goal was achieved in part by utilising a reference fluid. Laboratory results were required to fall within 6% of the specified evaporation loss of this reference oil before accepting results from a given Noack apparatus. At the same time, improvements and consistency were brought to the original Noack apparatus.

As a consequence of this work, the precision limits of this Unified Test Method were much improved over the prior DIN

51.581 method and the test became the CEC L-40-T-87, first published in 1987.³ This method is currently in use in many manual and automated Noack evaporative tests.

Other volatility methods

Other early approaches for determining volatility have been various forms of distillation, such as ASTM D 1160-87,⁴ published in 1951, and simulated distillation using gas chromatography (GC) such as ASTM D 2887-89,⁵ published in 1970. The latter is a technique using a temperature ramp to imitate the results of distillation. In particular, the simulated distillation value at 371°C (700°F) is frequently used because of the prior importance of this temperature in appraising lubricant volatility using actual distillation.

The precision of GC has always been one of the attractive features of the method. For this reason (as well as the comparatively greater difficulty in running the Noack Volatility Test), many laboratories, including our own, have placed dependence on GC for determining volatility.

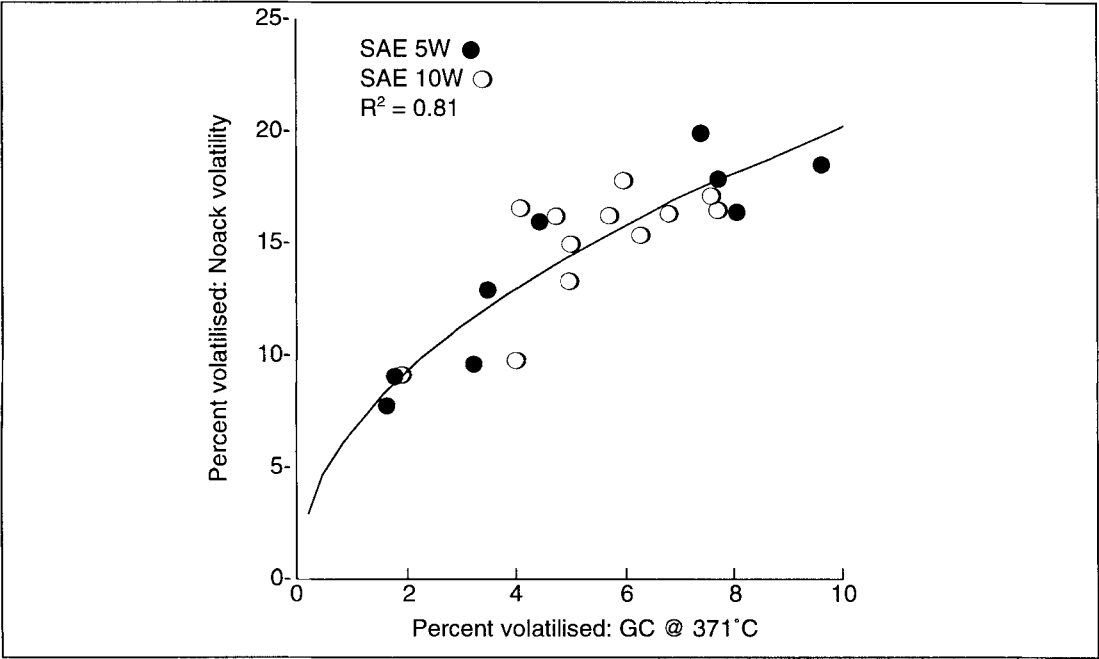
However, upon evaluating the similarities and differences among results from Noack tests and those from the ASTM D 2887 (GC-simulated distillation at 371°C), the data convinced us that, despite the precision of gas chromatography, the Noack test gave information not produced by simulated distillation. We found that while the two could be shown to have a strong relationship (as seen in **Figure 2**, overleaf), the relationship was not linear and it would not be expected that oxidation and thermal effects would be the same in the GC as in the Noack Volatility Test.

Collection of Noack volatiles

If, then, the Noack test gives a unique view of the volatility response of the engine oil, could this view be expanded to garner other information carried by the volatile products of the test? Would such information be pertinent to understanding the effects of engine oil volatility on the engine and catalytic converter?

Specifically, we felt that an important aspect of the volatilisation process had not been incorporated into the Noack Volatility Test. That previously unincorporated aspect was the collection and analysis of the volatile products of the Noack technique – oil volatilisation. This was the principal challenge once we were convinced of the value of the Noack approach. Accordingly, we set about redeveloping the method to incorporate a means of carefully collecting the volatile products.

Figure 2 Noack correlation with GC at 371°C



Concerns with the use of Wood's Metal

In addition, we considered that use of Wood's Metal was too hazardous to consider using in laboratories today. Chemical safety data^{6,7} suggest that the components of Wood's Metal can readily be toxic.

Inhalation of cadmium and lead pose several health risks including brain damage, renal dysfunction, broncho-pneumonia, and cancer. The composition and some of the hazards are shown in **Table 1**.

Table 1 Composition and properties of Wood's Metal

Element	Percent of eutectic ⁸	Boiling point of pure metal ⁹	Boiling point of oxide ⁹	TVL-air** (safe levels) ^{6,7}	Hazards ^{6,7}
bismuth	50	1560°C	180°C(dec.)*	?	non-toxic?
lead	25	1744°C	290°C(dec.)	<150 µg/m ³	brain damage
cadmium	12.5	765°C	~900°C(dec.)	<50 µg/m ³	carcinogen
tin	12.5	2270°C	~1800°C(subl.)†	<2000 µg/m ³	non-toxic

*decomposes **threshold limit value †sublimes

Focus of this paper This paper will

- detail the development and form of the modified Noack apparatus
- examine the correlation between the present Noack and our modified version
- present some of the data gained on the properties of the volatile products of several engine oils, and
- examine some of the implications.

To prevent confusion, in the following paper the earlier, Wood's-Metal-dependent apparatus will always be called by the term 'Noack' while our apparatus will be indicated by the term 'modified-Noack'.

*PROCEDURAL
IMPROVEMENTS
Elimination of
Wood's Metal*

As mentioned earlier, considering the operator hazards involved, elimination of the need for Wood's Metal became a first objective in our work.

Accordingly, we chose a new type of heater made of a noble metal fused directly to a suitable glass container. This form of heating gave no hot spots, but rather the smooth, even heating of the container found by using Wood's Metal.

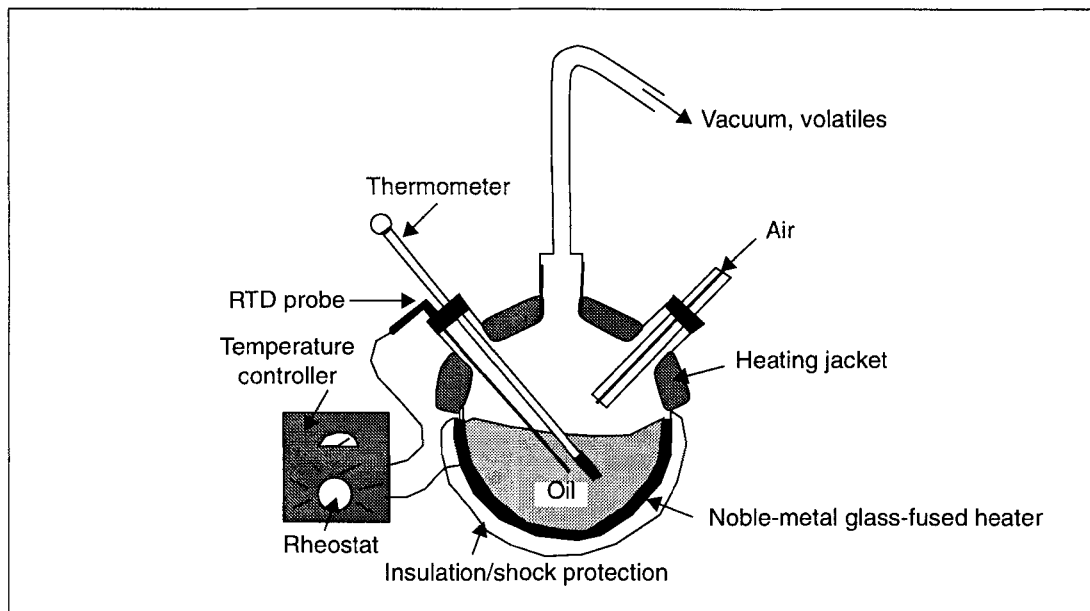
The noble metal surface is insulated and shock-protected by a covering of silicone rubber glass cloth mesh moulded to the flask. Relatively low-voltage electrical energy to the resistive surface is controlled and modulated by a console containing an electronic temperature controller and a voltage-limiting rheostat for fine adjustment of flask heating. Glass provided a variety of configurations, was relatively inert and free of catalytic effects, and could be readily cleaned with simple physical and chemical techniques.

Considering these aspects, we chose a volatilisation cell composed of a round-bottom, three-necked flask, the lower half of which was covered and heated by the fused-metal assemblage, as shown schematically in **Figure 3** (see overleaf).

Direct temperature control

As shown in **Figure 3**, in the modified-Noack, oil test temperature is signalled and controlled at the required 250°C by an RTD immersed directly in the oil rather than in the external source of heat as in the Noack apparatus. As with the Noack's Wood's Metal

Figure 3 Noble-metal glass-fused heater modified-Noack volatility cell

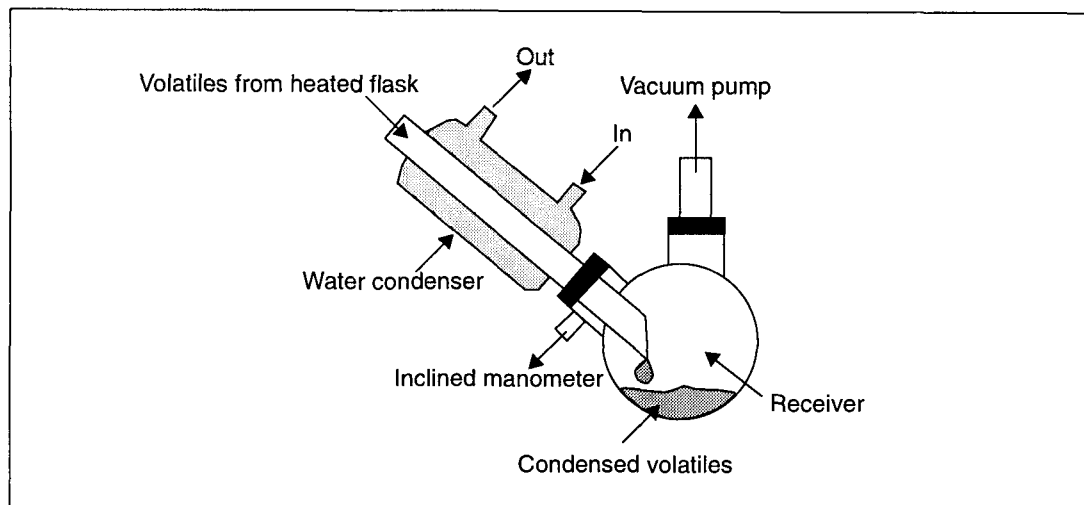


heating, the modified-Noack is essentially free of hot spots. A direct-reading mercury thermometer is used as an absolute back-up to assure the temperature of test. This thermometer is periodically checked for accuracy.

The air required to sweep the flask chamber under the slight vacuum imposed is introduced by a specially chosen glass capillary whose length was sufficient to be brought within 20 mm of the heated oil surface. It was recognised that the amount of air required to sweep the chamber at the appropriate rate is a function of the capillary diameter, the vacuum imposed, and the surface area through which the level of energy supplied by the heat drives the molecules forming the volatile products.

Using the required 65 grams of oil and keeping the level below the shoulder of the glass-fused heating area, the size of the special flask used in this work was chosen to provide approximately the same oil surface escape area for volatile components as that of the stainless steel Noack volatilisation vessel schematically shown in **Figure 1**.

To control the flow of volatiles up and over to the condensing area, a heating jacket maintained at an elevated temperature

Figure 4 Volatiles condensation and collection

(240°C), is placed over the top of the reaction flask, as is also shown schematically in Figure 3.

Volatiles collection

A number of factors were considered in choosing the appropriate approach to collecting the volatiles. Chief among these were the mode and temperatures of condensation.

Figure 4 schematically shows the primary condenser and volatiles receiver. Both are made of glass with ground joints.

The receiver is placed in a solid CO₂/propanol bath and the combination of this and the water condenser preceding it is quite effective in 'knocking-down' and trapping most of the volatiles. Further work is under way to make this section of the modified-Noack apparatus even more effective in trapping volatiles.

Other areas of change

In contrast to the Noack apparatus with its precise lengths and angles of glass tubing, the modified-Noack apparatus uses 4 mm internal diameter flexible plastic tubing to replace the 2 mm tubing specified by the CEC method. This replacement was found desirable since wider diameter tubing eliminates vacuum pressure problems from lines that become partially plugged by condensing oil vapours.

A number of other changes were incorporated and this is partially apparent in the overall schematic diagram of **Figure A1**,

p. 31. Although it may not be evident from the diagram, flexible tubing is used throughout the apparatus. No attempt was made to automate the apparatus since, after initial setting of the vacuum and readjustment within the first 5-10 min, the vacuum holds very steady during the remainder of the test.

Although the present work is indicative of the precision of the present prototype, work is continuing to simplify the design even further.

<i>Technique</i>	<i>Protocol</i> An abbreviated protocol used with the modified-Noack is given in Appendix 1 (see p. 30). This technique for the modified-Noack has proven very useful in the typical laboratory environment, especially with its elimination of the use of Wood's Metal.
------------------	---

<i>RESULTS: Modified-Noack precision</i>	As previously mentioned, it was hoped that the modified-Noack apparatus would not only have good repeatability but would substantially agree with the earlier Noack device.
--	---

Repeatability First results in a study of repeatability using the CEC Noack reference oil RL-N early in the development of the modified-Noack were encouraging. **Figure 5** shows the repeatability at somewhat higher vacuum than later used.

It is evident from **Figure 5** that the volatility values given by the modified-Noack, although higher than the reference value, show reasonable consistency and, at $\pm 4.0\%$ are well within the $\pm 4.6\%$ repeatability shown by the CEC round robin.

After further development, the repeatability of the modified-Noack was reappraised over a period of time. Results from this second study are shown in **Figure 6**.

Here it is evident that although the results are somewhat less repeatable ($r = 6.5\%$ – a consequence not of applying a repeatability test, but, rather, of extending the time over which the data was collected), the average value is quite close to the reference value (avg. = 14.87% *v.* std. = 14.9%). During this developmental work, we found a number of factors which affected the repeatability of the technique. Control of these factors was incorporated in the later designs.

Correlations Comparison was made between results obtained in another commercial laboratory using the Noack apparatus and

Figure 5 First study of repeatability

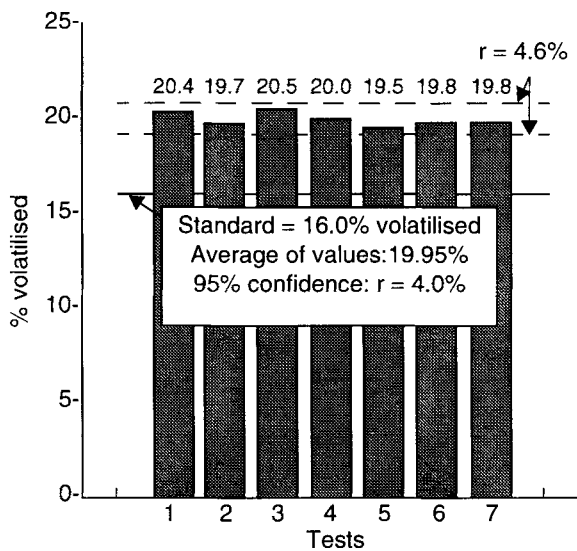


Figure 6 Second study of repeatability from laboratory quality assurance data

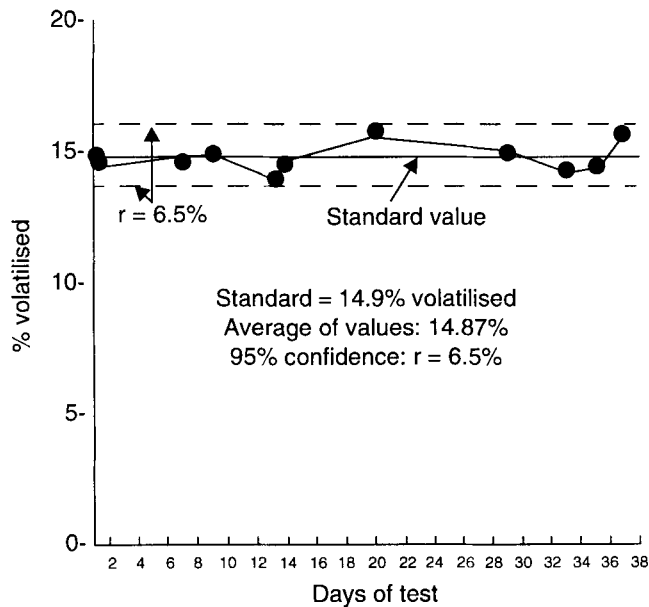
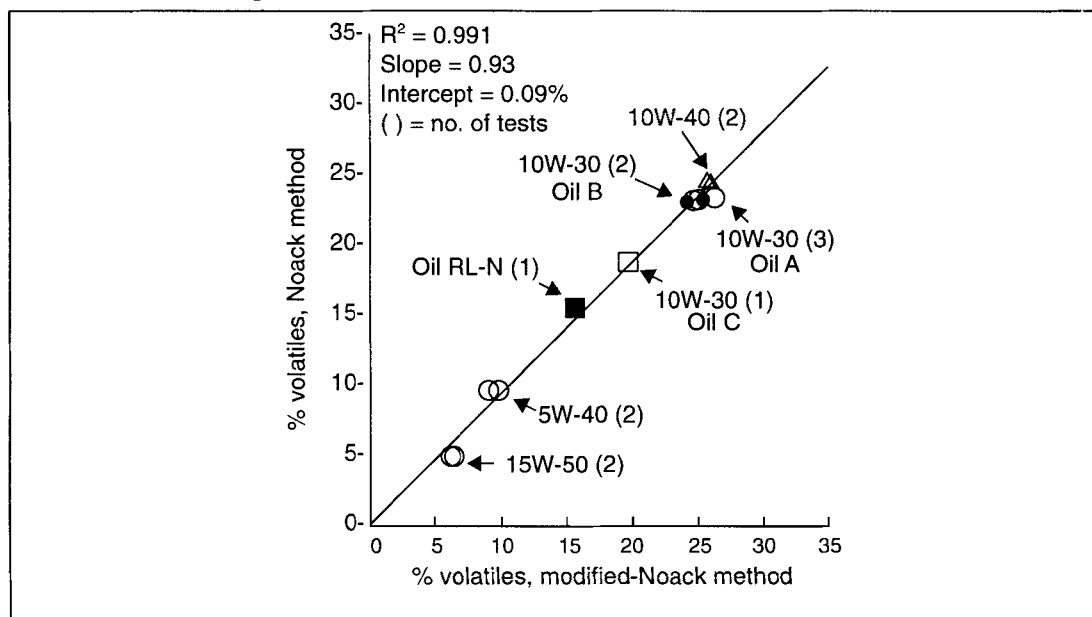


Figure 7 Correlation of Noack and modified-Noack results



procedure and results obtained on the same oils using the modified-Noack. **Figure 7** shows this information.

Correlation between the Noack and the modified-Noack is good with $R^2 = 0.991$, the slope almost unity (0.93), coupled with a low intercept value of 0.09% volatilised. Moreover, this correlation covers a fairly broad range of volatility – from approximately 5%–30%. Of equal interest is the fact that the engine oils used in the study shown in **Figure 7** are composed of a range of products of both natural and synthetic base oil formulation.

It is also encouraging that this close correlation between the Noack and the modified-Noack in **Figure 7** extends over a range considerably broader than the 10%–20% range within which the precision of the Noack test was developed by the Unified Method Study Group and published by CEC. Thus, it would seem that both the Noack and the modified-Noack have promise in having extensibility beyond the range used in the round robin.

Engine oils tested

With repeatability and correlation with the Noack established, the next area of our effort was to determine the characteristics of the

Table 2 Engine oil identification

Sample no.	SAE grade	Synthetic?
1	30	no
2	15W-40	yes
3	10W-40	yes
4	5W-30	no

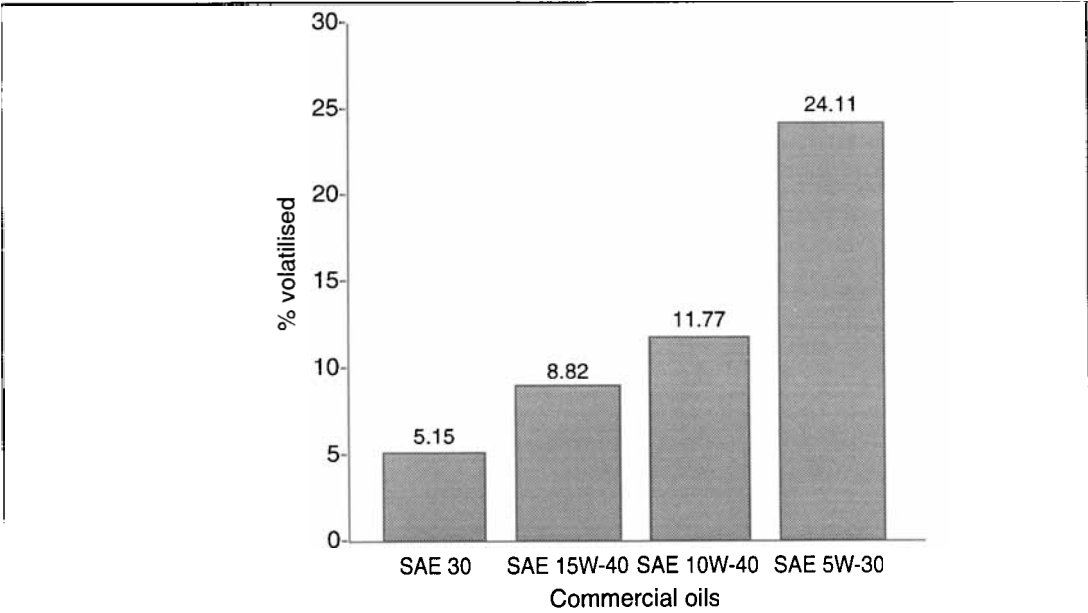
volatiles and compare these to the ‘pot residues’ of several representative engine oils.

The commercial engine oils chosen for this portion of the study are identified in **Table 2** and were chosen for their range of base stock characteristics.

Results of volatilisation

The four oils were volatilised in the modified-Noack and the weights of the samples in the volatilisation flask were obtained by weighing the flask plus oil before and after volatilisation. Results are shown in **Figure 8**.

Figure 8 Percent volatilised of four chosen commercial engine oils



**Results of analyses of
volatiles and residues**

Gas Chromatography Gas chromatography (GC) is a very informative method of determining the general molecular composition of an oil. In addition, it requires very little sample – normally in microlitres.

Noack reference oil In **Figures 9a-c** the results of gas chromatographic analysis of the Noack reference oil are shown using the technique of ASTM D 2887. The start of each chromatogram is the vertical line on the left and the height of the curve progressing to the right indicates the increasing complexity and molecular weight (Mw) of the oil. For the Noack reference oil it is evident from the 'bell'-shaped curves that the oil is mineral in nature.

Of greater importance is the fractionation of the Noack mineral oil that has occurred during volatilisation. By referring to the vertical line drawn from the curve for the fresh oil in **Figure 9a**, this vertical line is extended through the GC curves of **Figures 9b** and **9c** as a reference line. So, in comparison to the fresh oil in **Figure 9a**, the chromatogram of the residue in **Figure 9b** shows the residue to be slightly higher in molecular weight distribution after volatilisation and, in **Figure 9c**, the volatile portion is obviously lower in Mw distribution.

Volatiles from this CEC, 16.0% Noack reference oil, amounted to 15.52%.

It should be noted that in obtaining the chromatograms of **Figure 9**, and those that follow in this paper, the normal dilutions of test oils for gas chromatography (one part sample in 10 parts diluent) were altered to obtain these proportional chromatograms. That is, as shown in **Figure 9**, the fresh oil was diluted normally; the volatile product was diluted to 15.5% of the fresh oil and the residue was diluted to 84.5% of the fresh oil.

SAE 30 engine oil The results of the test on the SAE 30 oil given in **Figures 10a-c** (see overleaf) showed very little volatility, 5.15%, as was previously noted in **Figure 8**. The chromatogram of the volatiles barely rises above the base line. Comparing the distribution curves of the fresh SAE 30 to that of the fresh Noack reference oil, it is evident that the peak of the curve is at higher Mw/complexity for the former oil.

It may be observed in **Figure 10c** that there is an evident but small (in this proportional GC) sign of lower Mw components of the oil coming over in the volatiles. Chromatograms shown in **Figures 14a-d** (see p. 22) will give detail to this observation.

Figure 9 Gas chromatograms of the three components of a modified-Noack test of the Noack reference oils at dilutions proportional to their fraction of the fresh oil

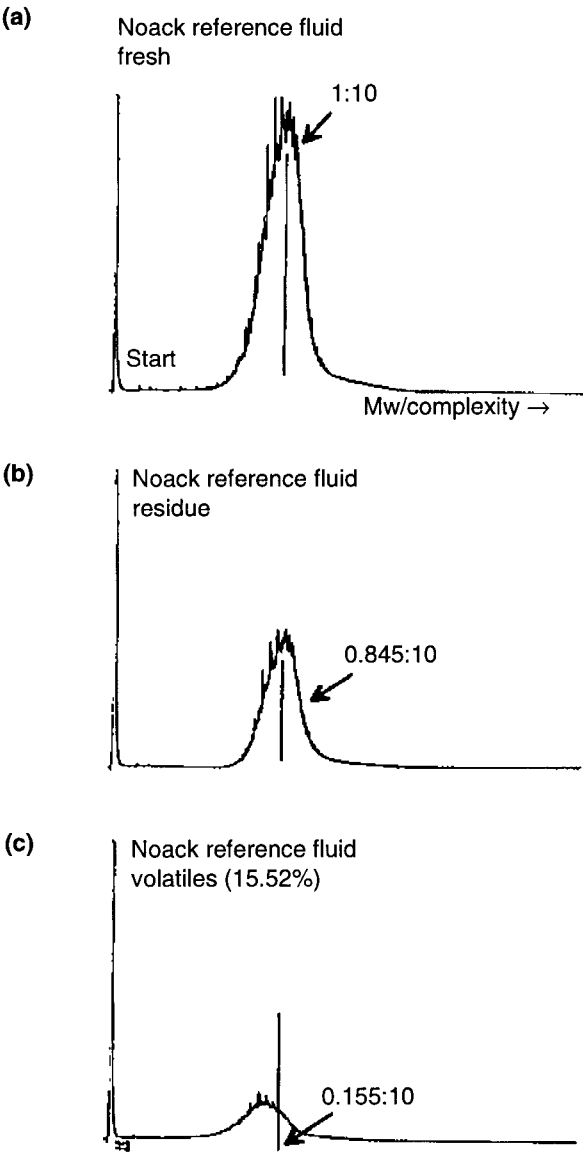
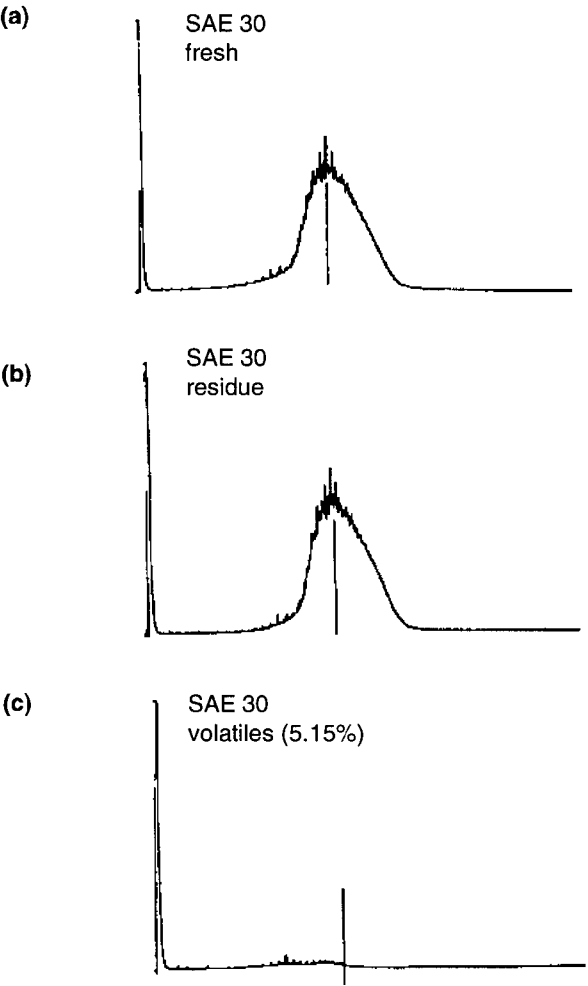


Figure 10 Gas chromatograms of the three components of a modified-Noack test of the SAE 30 engine oil



As with the Noack reference oil, the GC distribution curves for **Figure 10** indicate that the base oil is mineral in nature.

SAE 15W-40 engine oil Results of the GC analyses of the 15W-40 oil in **Figures 11a-c** (see overleaf) show the multiple peaks and non-bell-shaped distribution typical of synthetic base oil. It is also evident that volatiles lost from the fresh oil are mainly from the earliest Mw peak (shown by an arrow in the fresh oil chromatogram, **Figure 11a**). The GC of the volatiles fraction, **Figure 11c**, shows some of this peak, and there is a matching reduction in the area of this peak in **Figure 11b**.

While this series of chromatograms again illustrates the relatively higher evaporation loss of the light ends, it also shows some volatilisation of certain very narrow Mw, heavier fractions having high initial concentrations.

SAE 10W-40 engine oil The chromatograms of this oil shown in **Figures 12a-c** (see overleaf) have some of the multiple peaks associated with oils containing or composed of synthetic oils.

In these analyses it is again evident that the volatiles produced reflect the lower Mw/complexity components of the engine oil, as shown by the arrows in **Figures 12a** and **c**.

One of the reasons for believing that this engine oil is formulated with a combination of both mineral and synthetic oils is the bell-shaped configuration of the volatile product. The fact that there are two very evident peaks shown by the fresh and residual oils is strong evidence that the engine oil is a parasynthetic.

SAE 5W-30 engine oil The GC curves in **Figures 13a-c** (see p.20) are classic bell-shaped curves typical of mineral oils. Again, there is the tendency for fractionation shown with the Noack reference oil.

The relatively high level of volatilisation shown by this 5W-30 is reflected by three indicators:

1. The decreased size of the residue bell curve
2. The increased size of the volatiles bell curve, and, most particularly
3. The shifts in the MS/complexity distribution for the three samples shown by the vertical line from trace to trace.

Closer view of volatiles In the previous **Figures 10-13**, GC information carried by the volatiles was restricted by showing the

Figure 11 Gas chromatograms of a modified-Noack test of the SAE 15W-40 synthetic engine oil

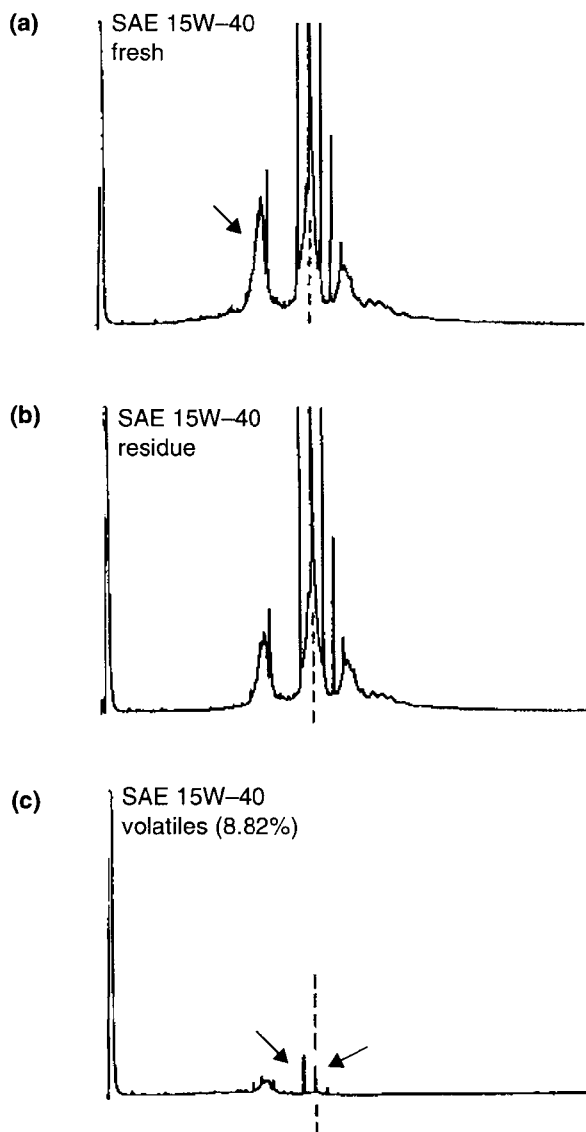


Figure 12 Gas chromatograms of a modified-Noack test of the SAE 10W-40 synthetic or parasyntetic engine oil

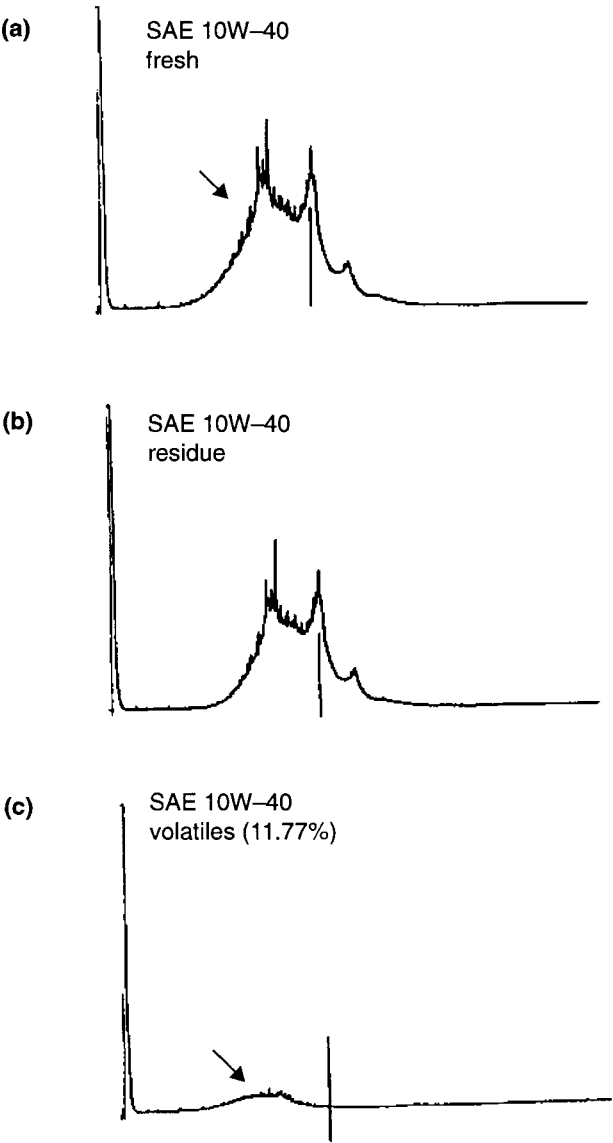
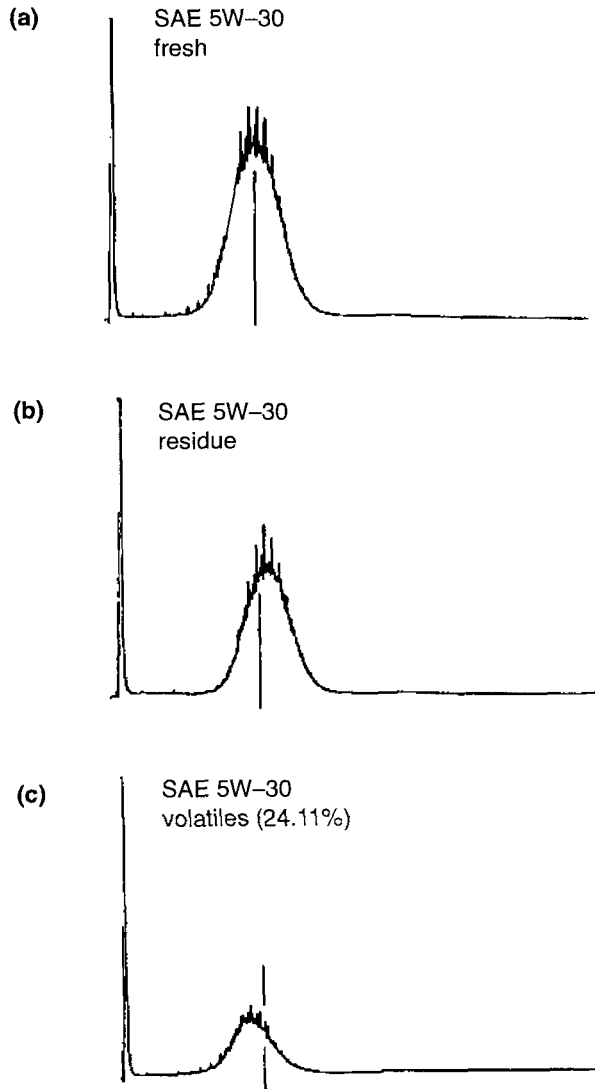


Figure 13 Gas chromatograms of a modified-Noack test
of the SAE 5W-30 mineral-based engine oil



chromatograms of volatiles at concentrations proportional to the volatile fraction of the fresh oil. However, volatiles can be appraised for the information they carry by GC analysis at normal concentrations (1:10, sample:dilution). The informational GC at 1:10 dilution is contrasted to the volatiles-proportional dilution in **Figures 14a-d** (see overleaf).

The more detailed, 1:10 dilution, GC data on the volatiles presented in **Figure 14** brings out several items of information on the four commercial oils tested with the modified-Noack procedure. For example, the volatile products of the SAE 30 oil shown in **Figure 14a** give evidence of being generated from a bi-modal distribution of hydrocarbons – typical of a blend of mineral base oils. **Figure 14b** shows that the volatile products from the SAE 15W-40 are from a synthetic oil with perhaps a small amount of higher-volatility mineral oil present. The mineral oil components of the parasyntetic SAE 10W-40 stands out in the volatile products GC of **Figure 14c**, and this can be identified to some degree with the mineral oil GC of **Figure 14d**.

*Spectroscopy of additive
metals and phosphorus
by ICP*

Since phosphorus in general and ZDDP (the zinc di-organo dithiophosphates family of additive metallo-organics) in particular, were under question regarding their effects on the automobile's catalytic converter, we next sought to obtain information on these and any other metallo-organic compounds used as oil additives in the fresh oils. A particularly interesting question was: would such additive components be left in the residue or would they also be part of the volatilised product?

Analysis of the Noack reference oil The analysis of the Noack reference oil plotted in **Figure 15** (see overleaf) showed very low levels of metallo-organics – no more than 40 ppm of any of the five more important metal elements plus phosphorus. Most concentrations were less than 10 ppm, which places something of a limit on interpretations. Nonetheless, the data seemed to indicate that there are some metallo-organics in the volatiles and that the element second most evident in the volatiles was phosphorus. This tentative data made it even more interesting and important to determine the response of the fully formulated engine oils.

It should be noted that the elemental concentrations given for residue and volatiles components in **Figure 15** are from 1:10

Figure 14 Gas chromatograms of the volatile components of the four commercial engine oils at two levels of concentration

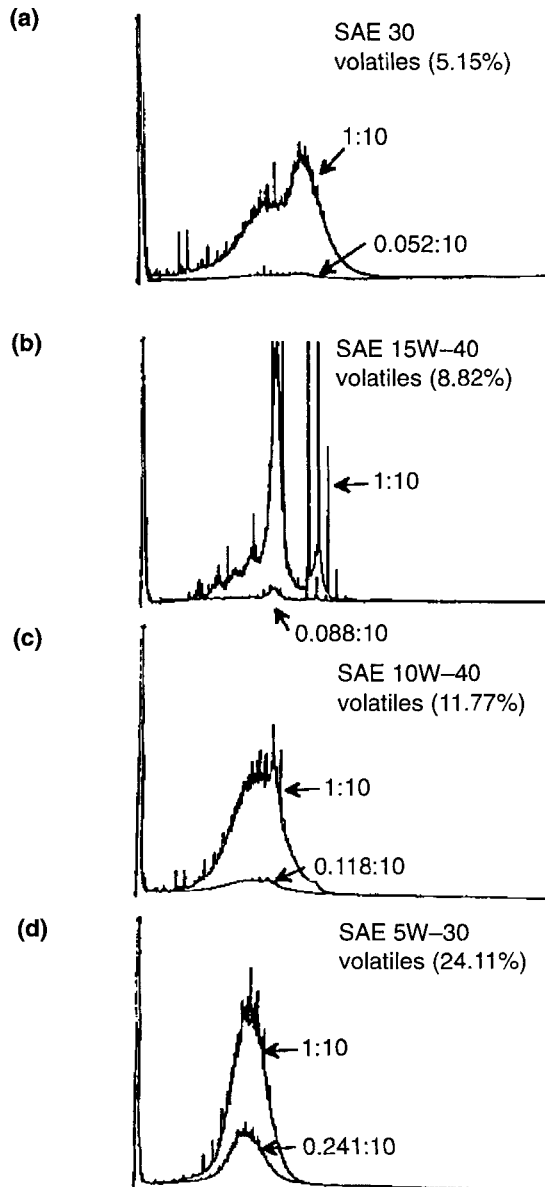
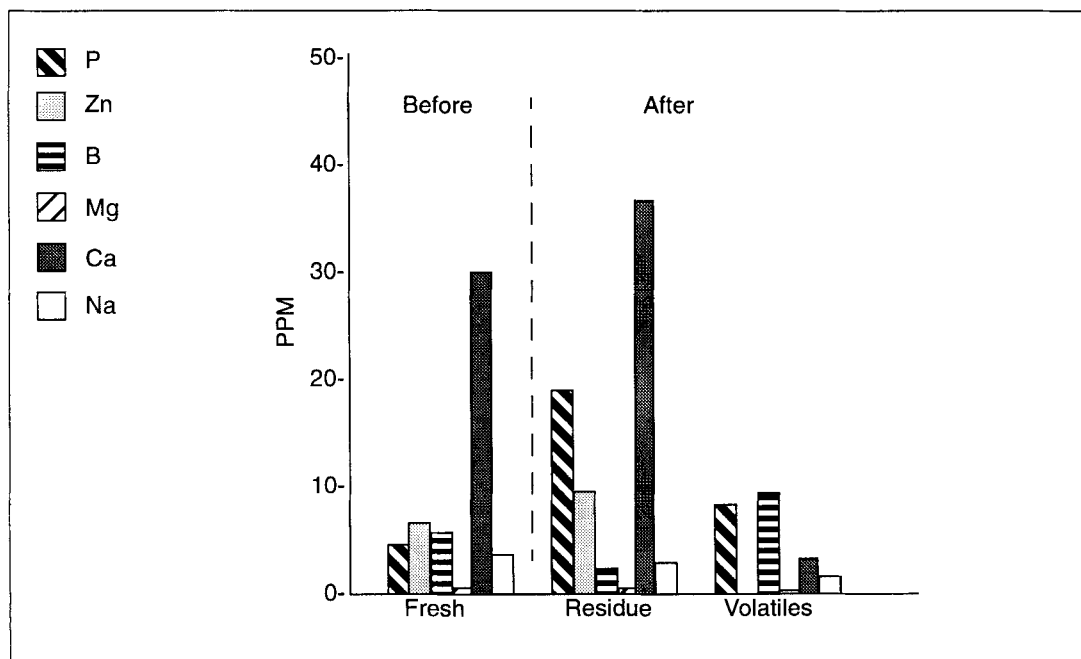


Figure 15 Results of ICP analyses of the three samples of the Noack reference oil before and after volatilisation

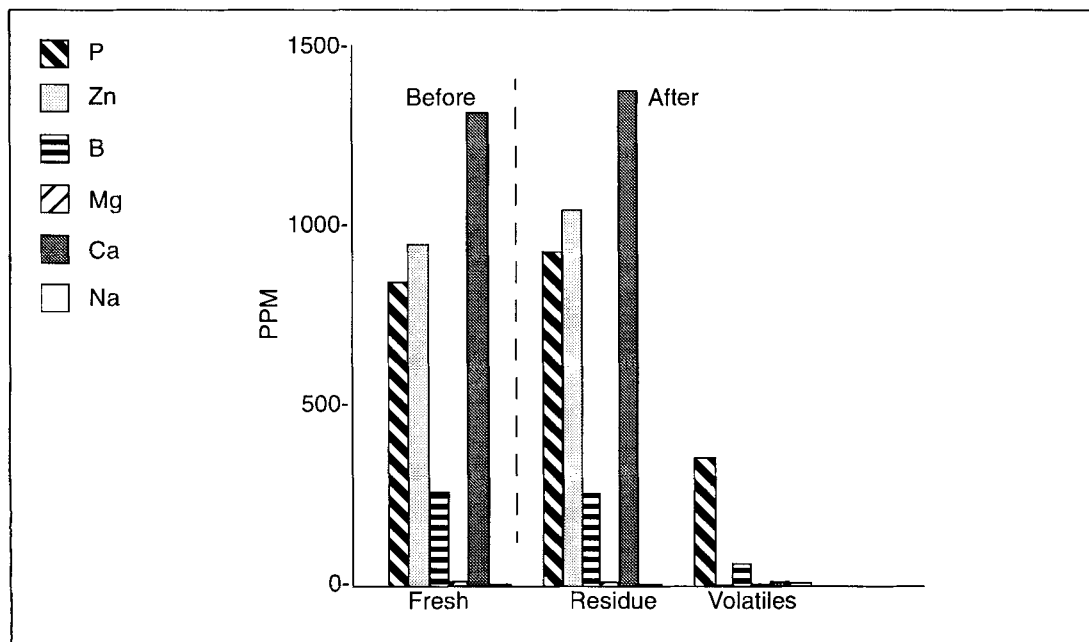


dilution ratios in each case. Thus, they are not additive. For example, the sum of calcium in the residue and the volatiles should not be expected to add up to the calcium in the fresh oil. In fact, it is evident that, not surprisingly, the elements analysed generally seem to be somewhat more concentrated in the residue than in the original fresh oil as a consequence of loss of the volatiles, which are mostly base oil.

Analysis of the SAE 30 engine oil When the SAE 30 volatilisation results were examined, the data in **Figure 16** (see overleaf) were obtained. These data clearly show that phosphorus can be a significant part of the volatile products.

This was the first clear evidence that phosphorus in some form or another was among the volatile components. Interestingly, zinc – usually closely associated with phosphorus in ZDDP – was not found in the volatiles of the SAE 30. It was also interesting to see that boron also accompanied the volatile products.

Figure 16 Results of ICP analyses of the three samples of the SAE 30 before and after volatilisation



Synthetic 15W-40 engine oil After the results of elemental analysis with the modified-Noack SAE 30 mineral-oil based product, it was of high interest to obtain elemental analyses for the SAE 15W-40. These are shown in **Figure 17**.

Again it is evident, to a lesser extent, that phosphorus is being brought over with the volatiles, while zinc is not.

Parasynthetic SAE 10W-40 engine oil Elemental analysis with the ICP on the modified-Noack test oil samples from the apparently parasynthetic SAE 10W-40 engine oil is shown in **Figure 18**.

Once more, phosphorus is shown to accompany the volatiles – as does boron (as before in the findings from the ICP analysis of the volatiles from the SAE 30 engine oil shown in **Figure 16**).

SAE 5W-30 engine oil Elemental analysis of the SAE 5W-30 mineral-oil-based engine oil is shown in **Figure 19** (see overleaf).

In this analysis only a relatively small concentration (16 ppm) of phosphorus was noted in the volatiles. If this was an

Figure 17 Results of ICP analyses of the three samples of the SAE 15W-40 before and after volatilisation

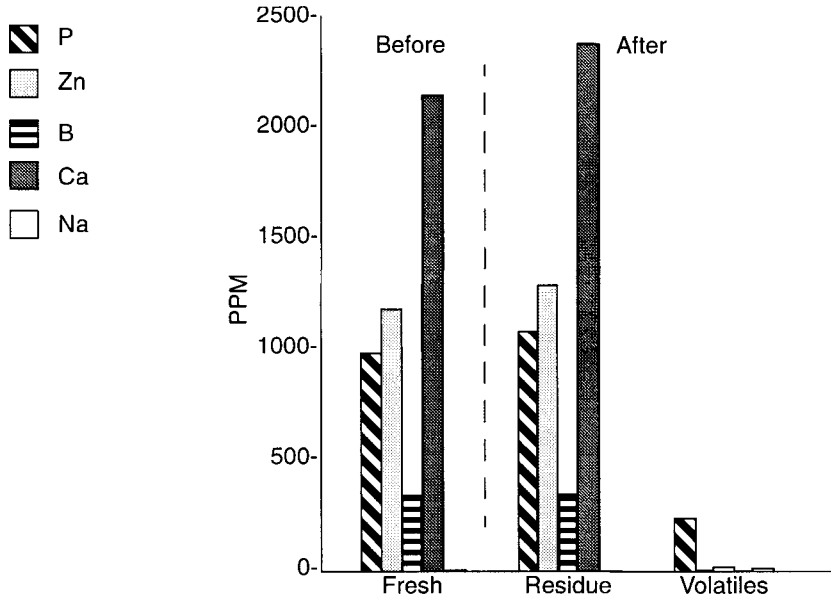


Figure 18 Results of ICP analyses of the three samples of the SAE 10W-40 before and after volatilisation

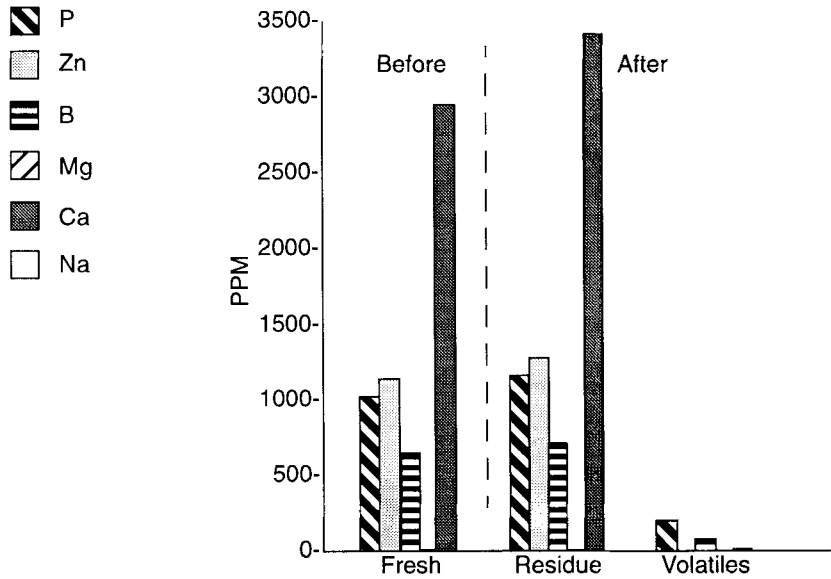
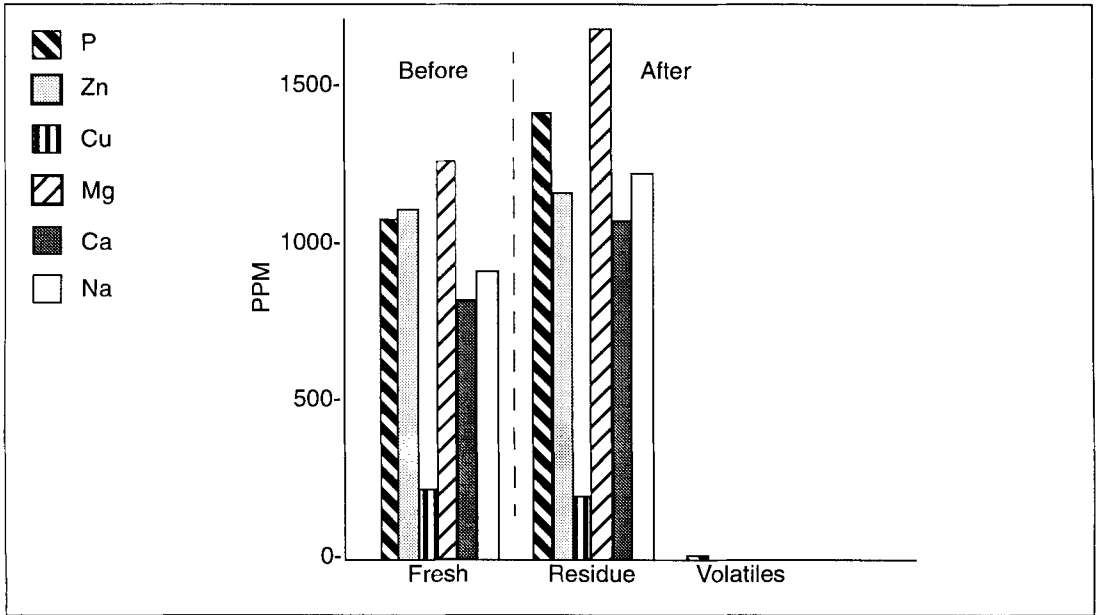


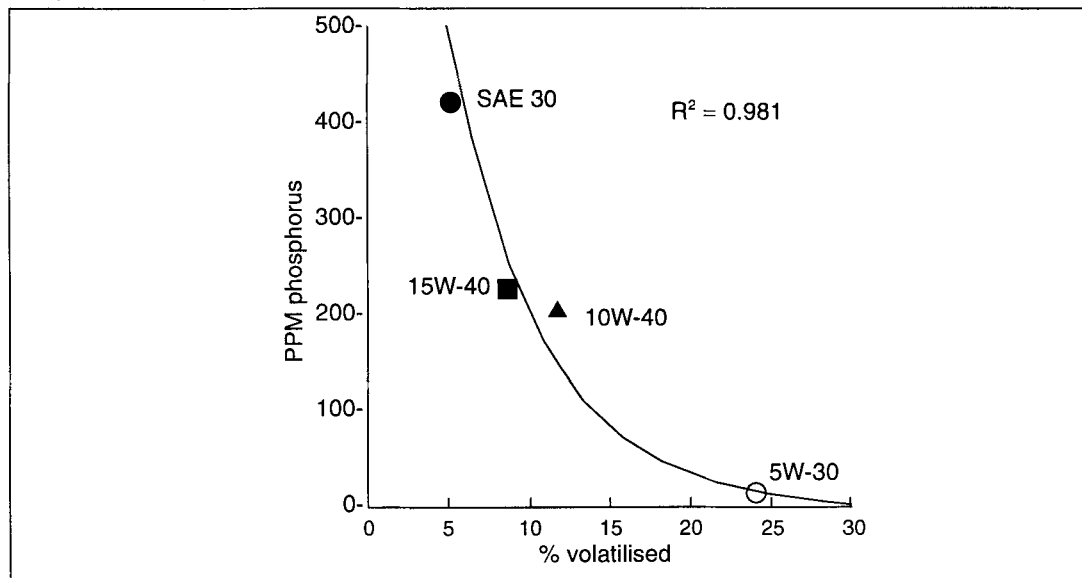
Figure 19 Results of ICP analyses of the three samples of the SAE 5W-30 before and after volatilisation



effect of high volatility in which the amount of phosphorus was diluted by the relatively large level of volatile product, it would have interesting volatility control implications.

Discussion of ICP results In the ICP analysis of each oil, as has been already noted, it is evident from **Figures 16-19** that the concentration of the metal elements is greater in the residue than in the fresh fluid. This would be expected as a result of the volatilisation of a higher proportion of hydrocarbons than metallo-organics. Phosphorus is the most evident element in the volatiles, followed by boron when present in the fresh oil at sufficient levels (the SAE 5W-30, for example, contained no boron).

Phosphorus in the volatiles In the analyses of the volatiles from the modified-Noack tests, the ICP data on the fresh oil, residue, and volatiles point to two interesting observations. First, the finding of phosphorus in the volatiles without the simultaneous presence of zinc indicates the breakdown of at least some of the commonly

Figure 20 Crossplot of phosphorus concentration in volatile samples and the percent volatilised

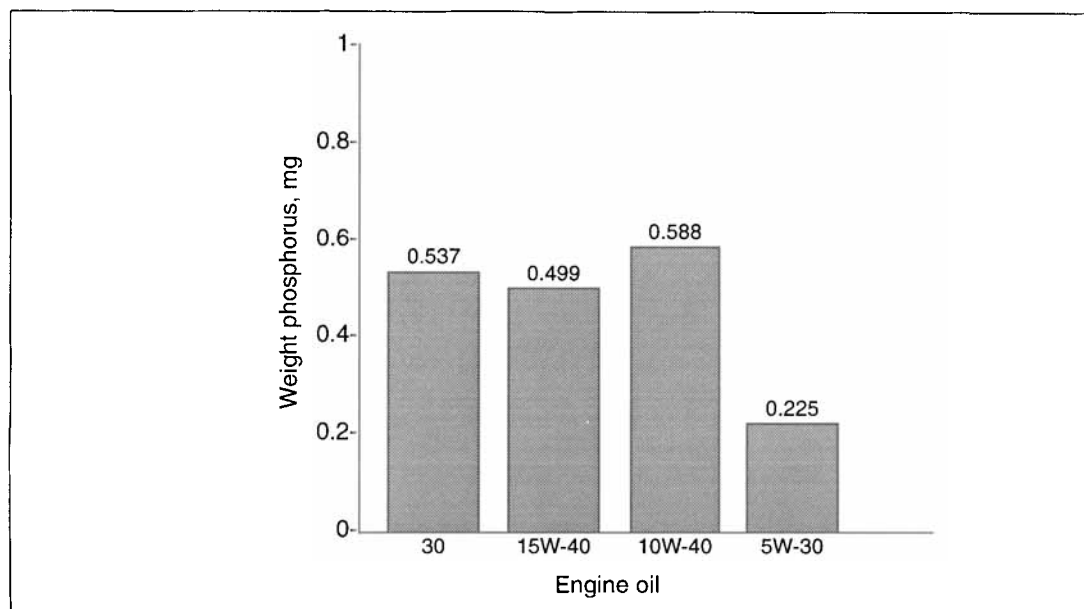
present ZDDP anti-wear/anti-oxidant additive under the test conditions.

The second and more significant aspect of phosphorous volatilisation is in regard to the concerns about the effects of this volatilised phosphorus on emissions. Reaction of phosphorus with the aluminium in the catalytic converter forms an aluminium phosphate salt which can occlude the pores and render the surface of the catalytic converter unable to adsorb the volatile hydrocarbons. The catalyst is then poisoned, no conversion takes place and emissions are not controlled.¹⁰

In the modified-Noack studies of the four engine oils, the ICP data indicated that the concentration of phosphorus in the volatiles decreased with increasing volatility, as shown in **Figures 16-19**. This raised the question of whether the amount of phosphorus brought over with the volatiles was constant with time of test exposure. A graph of phosphorus concentration versus percentage volatiles is given in **Figure 20**.

It is shown in **Figure 20** that the concentration of phosphorus in the volatiles varied inversely and exponentially with the percent volatilised with a relatively high correlation of $R^2 = 0.981$. This perhaps suggested that the amount of phosphorus being

Figure 21 Comparison of total phosphorus weight in volatile samples from modified-Noack tests



generated in the volatiles was time dependent if the concentration of ZDDP were sufficient in the fresh oil. With this reasoning, a weight comparison of the amount of phosphorus in the volatiles of the four engine oils tested was quite interesting and the results are shown in **Figure 21** and **Table 3**.

These data strongly indicate that the level of phosphorus in the volatiles is not a function of the amount or rate of volatilisation. Rather, the data suggest that the relatively constant weight of phosphorus in the volatiles is a function of some more constant process, perhaps involving the initial levels of phosphorus, but almost certainly involving the decomposition rate of the ZDDP used in these oils at the temperature of the Noack test. The fact that the level of phosphorus generated by the volatilisation of 5W-30 is about half that of the other three oils might reflect a different form of ZDDP, or it may be analytical error at the low, 16 ppm, level associated with the SAE 5W-30 oil.

In any case, it is of considerable interest that the relatively consistent amount of phosphorus in the volatile products gathered by the modified-Noack seems essentially independent of the degree of volatilisation of the engine oil. At this time such

Table 3 Phosphorus relationship

Oil	% vol.	ppm	Phosphorus levels, mg		
			Fresh	Residue	Volatiles
30	5.15	423	65.9	68.7	0.54
15W-40	8.82	231	58.3	63.9	0.50
10W-40	11.77	202	66.3	66.0	0.59
5W-30	24.11	16	70.2	70.0	0.22

results are too limited to draw far-reaching conclusions, but they certainly point to the need for further studies of the relationship between volatility and phosphorus concentrations in the volatilised product.

Other analytical studies

The ability to subject both the residue and the volatiles to different analytical techniques, such as infrared spectroscopy and sulphur and nitrogen analyses, was apparent. These additional studies also proved interesting and enlightening and the data will be published in a forthcoming paper.

CONCLUSIONS

1. A modification of the Noack Volatility Test has been developed which permits the collection of the volatilised products.
2. The modified-Noack eliminates the use of the health-hazardous Wood's Metal as a heat-transfer medium.
3. Correlation of the modified-Noack with the Noack is high, with a Coefficient of Determination, R^2 , of 0.991, a slope almost unity (0.93), and an intercept almost zero (0.09%).
4. Repeatability of first results with the modified-Noack showed a value of $\pm 4.0\%$ of the mean.
5. Day-to-day replication gave $\pm 6.5\%$ of the mean with a volatility mean of 14.87% for a Noack reference oil having a listed value of 14.9%.
6. A study was made of the residual and volatilised properties of four commercial synthetic, parasyntetic, and mineral oil base engine oils. These studies indicated that
 - (a) some phosphorus compounds in the fresh engine oil decompose and are found in the volatiles.

(b) the amount of phosphorus in the volatiles is independent of the volume of the volatile products.

7. Gas chromatographic studies showed that chromatograms of the volatiles could be of value in determining the nature of the fresh oil and the source of the volatiles.

Acknowledgements

We wish to thank the entire staff at Savant Laboratories, especially Brian Cluff and Penn Schloemann for their willingness to help whenever requested. We also wish to express our thanks to Kevin Wolfe from the Tannas Co. for his assistance with the computer sketch of the modified-Noack.

References

1. Noack, K., *Agnew. Chem.*, **49**, 385 (1936).
2. 'Determination of evaporation loss of lubricating oils (Noack Method)', DIN 51-581.
3. 'Evaporation loss of lubricating oils', CEC L-40-T-87, 1987.
4. 'Distillation of petroleum products at reduced pressures', ASTM D 1160-87.
5. 'Boiling range distribution of petroleum fractions by gas chromatography', ASTM D 2887-89.
6. *The Sigma-Aldrich Library of Chemical Safety Data*, ed. R.E. Lenga, pp. 201, 339, 1134, 1710, and 1841, Sigma-Aldrich Corp., 1985.
7. *The Merck Index*, Merck and Co., pp. 95, 45, 51, and 488 (1989).
8. Briscoe, H.T., *General Chemistry for Colleges*, Houghton Mifflin Co., Cambridge, Mass., p. 653 (1943).
9. *Handbook of Chemistry and Physics*, The Chemical Rubber Co., pp. B-73, 75, 102, and 149 (1970-1).
10. Summary statement from several technical publications and personal dialogue with knowledgeable individuals in the automotive field.

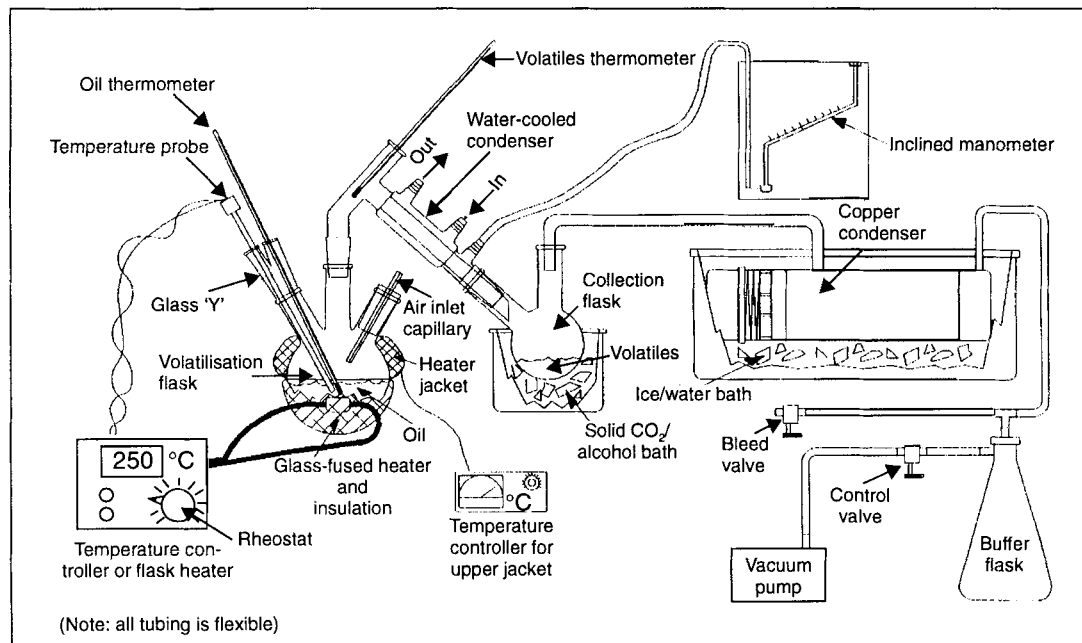
Appendix 1 Modified-Noack protocol per Savant: Preparation and care of apparatus

1. Clean all glassware with hexane to remove residual oil and acetone to remove moisture.
2. After every third run, rinse and dry all flexible tubing with hexane to remove any oil accumulation on walls of tubing.
3. After every 10 tests, disassemble the copper condenser and rinse thoroughly with hexane and acetone.

Setting up test

4. Obtain a tare weight for both the volatilisation and collection flasks.
5. Weigh 65.00 g \pm 0.05 g of sample into the volatilisation flask.
6. Assemble apparatus according to **Figure A1**. Grease all ground-glass joints with high temperature hydrocarbon grease.
7. Set temperature to 250°C for volatilisation flask and 240°C for top heating jacket. Approximately 15 min is required for the volatilisation assemblage to come to temperature. (Note that no vacuum is imposed and that this time of coming to temperature is not part of the test time).
8. Wrap aluminium foil around the arms of the volatilisation flask to help maintain the temperature of the volatiles and encourage their passage to the collector assemblage.
9. Surround glass collection flask (receiver) with solid CO₂ (so-called 'dry ice') in a propanol slurry. Cover assemblage with aluminium foil to insulate.
10. Chill copper condenser with a water/ice slurry.

Figure A1 Modified-Noack volatility apparatus per Savant

**Initiating test**

11. When the temperature of the oil in the volatilisation flask is at 250°C, turn on the vacuum pump and, using the needle valve, adjust the pressure quickly to 12 mm (water) vacuum measured on the inclined manometer.
12. Start the timer as soon as the pressure is correctly adjusted.
13. Monitor the pressure during the first 10 min of the test and make any minor pressure adjustments needed to maintain 12 mm (water) vacuum.

Completing test

14. After 60 min \pm 5 seconds, first turn off the vacuum, then, immediately afterward, turn off the volatilisation flask heaters.
15. Allow the vapours to condense before disassembling the volatilisation/condensing/collecting assemblage.
16. Follow established Savant laboratory practices to avoid adding or losing weight of either the volatilisation or collection flasks. Wipe ground-glass joint grease off carefully with hexane-moistened tissues.
17. Weigh both volatilisation and collection flasks when they have returned to room temperature.

Determining and reporting results

18. Calculate percentage volatilised as follows:
 $\% \text{ volatilised} = 1 - (W_t / W_i) \cdot 100$ in which W_t is the final weight of oil and W_i is the initial weight of oil.
19. Report percent volatilised to two decimal places.