

PEI Values at Ring Belt and Lower Engine Operating Temperatures

Studies of PEI of Fresh Engine Oil at Both Ring Belt and Lower Temperatures

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PEI Values at Ring Belt and Lower Engine Operating Temperatures

Phosphorus Emission Index data gathered until recently were all generated at ring belt temperatures ($\approx 250^{\circ}\text{C}$).

At the last meeting of the ILSAC volatility team, a question was raised about the relationship of PEI at 250°C (PEI_{250}) to its value at lower temperatures.

The question was interesting and thoughtful. It seems reasonable that phosphorus volatility and the mechanisms producing it might change with temperature.

The ring belt area is not the only possible source of phosphorus emissions and the bulk of the oil is always at considerably lower temperatures than the ring belt.

PEI Values at Ring Belt and Lower Engine Operating Temperatures

The information from engine studies also presented at the last meeting suggested measuring phosphorus emissions and related PEI at 165°C (PEI₁₆₅).

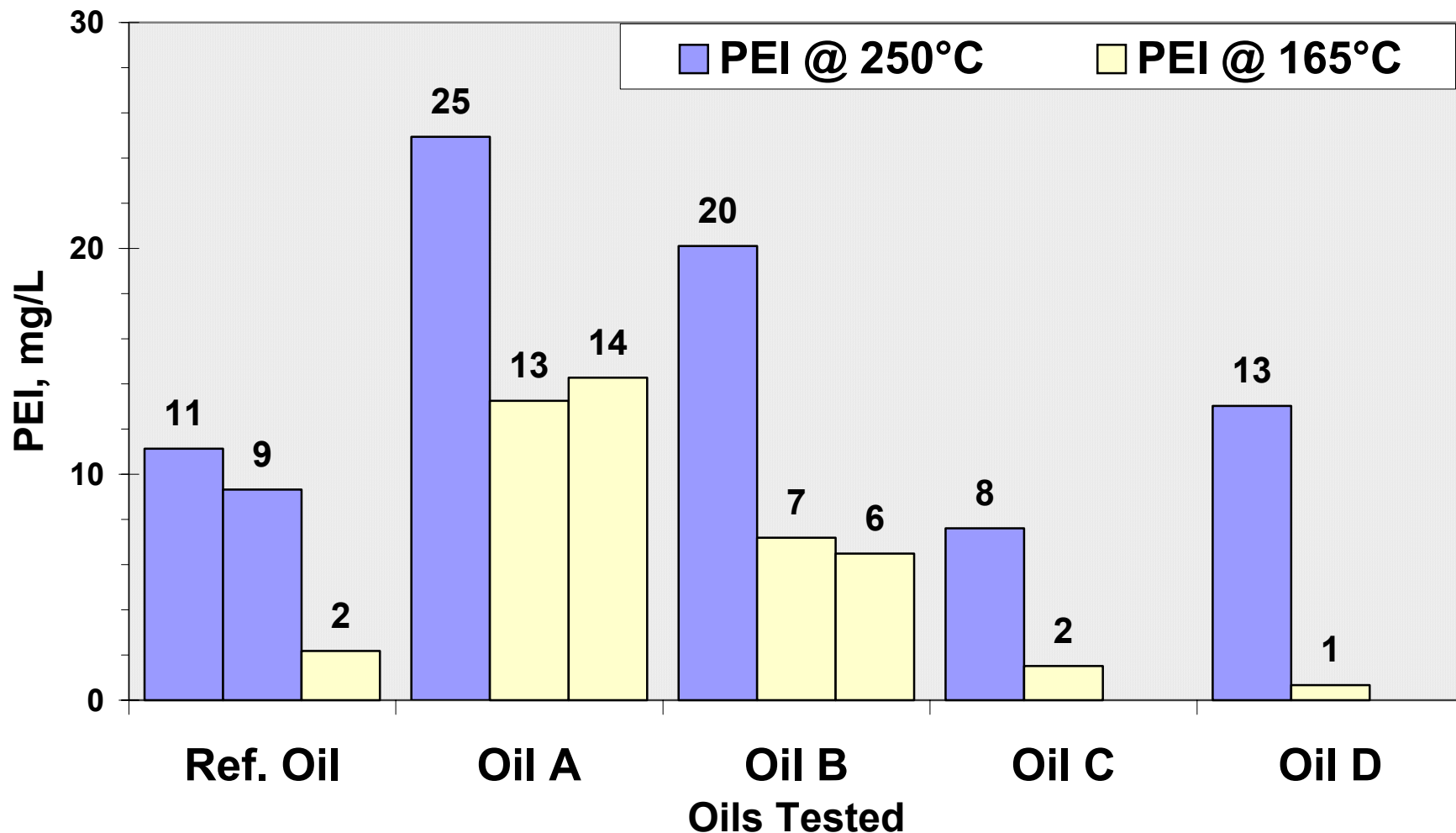
The technique to collect the volatile phosphorus at this lower temperature was simple, since PEI at any temperature is simply the mass of phosphorus in milligrams per Liter volatilized from a known mass of engine oil sample.

To provide enough volatilized material at 165°C, 10 mL of a more volatile, phosphorus-free hydrocarbon was added to the 65 g of engine oil sample.

The technique worked well and provided sufficient sample to determine the effects of temperature on PEI₁₆₅ to compare to PEI₂₅₀ – as well as to obtain NMR spectra to view change in the response of the phosphorus additive.

PEI Values at Ring Belt and Lower Engine Operating Temperatures

Comparison and Repeatability of PEI₂₅₀ and PEI₁₆₅ Values
For Engine Oils Having Moderate PEI₂₅₀



PEI Values at Ring Belt and Lower Engine Operating Temperatures

The data on Oils A, B, C, and D show that :

1. Phosphorus volatility and PEI decrease with decreasing temperature – sometime substantially.
2. The effect of lower temperature on phosphorus volatility is different for different oils.

This information led to the question of whether the mechanism for phosphorus volatilization changes at lower temperatures compared to higher temperatures.

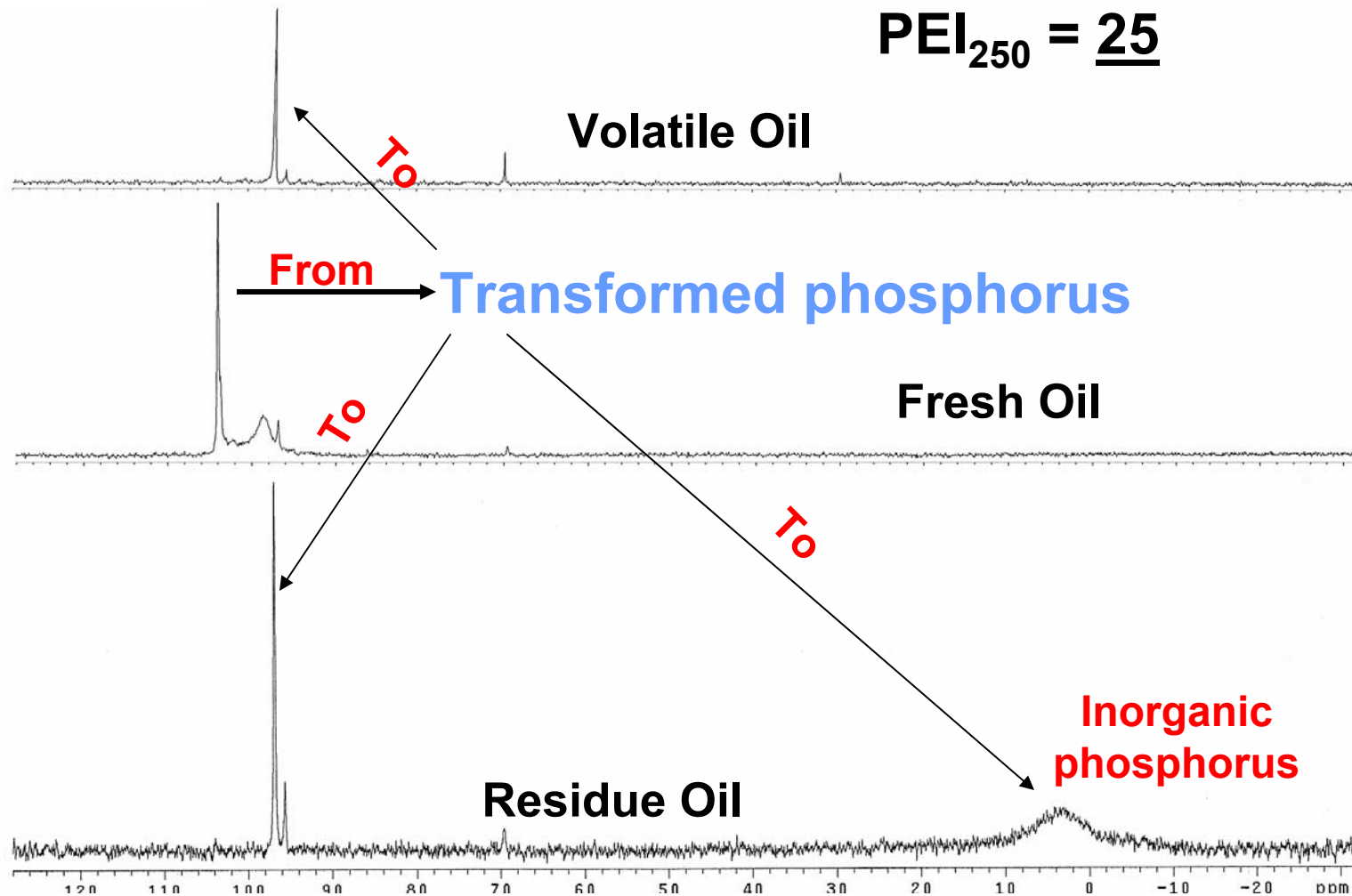
A recent paper* presented the nuclear magnetic resonance (NMR) spectra for the fresh, volatilized, and residual samples of Oils A, B, C, and D which had generated the PEI₁₆₅ and PEI₂₅₀. These NMR spectra are shown on the next slides.

* R.J. Bosch, et. al.. **"Continued studies of the causes of engine oil phosphorus volatility"**, SAE Powertrain Meeting, San Antonio, Oct., 2005.

PEI Values at Ring Belt and Lower Engine Operating Temperatures

NMR analysis of Oil A @ 250°C

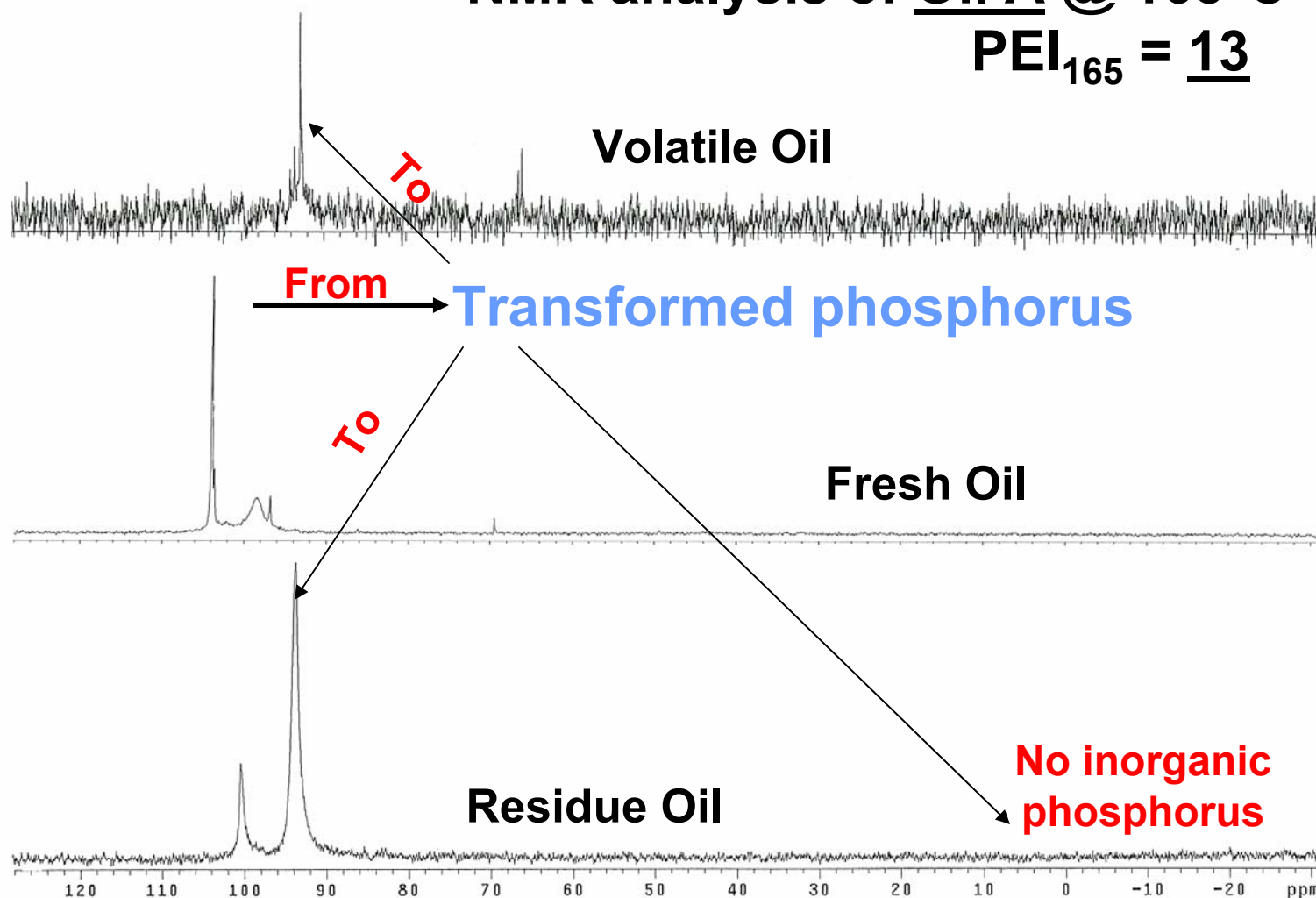
$$PEI_{250} = \underline{25}$$



PEI Values at Ring Belt and Lower Engine Operating Temperatures

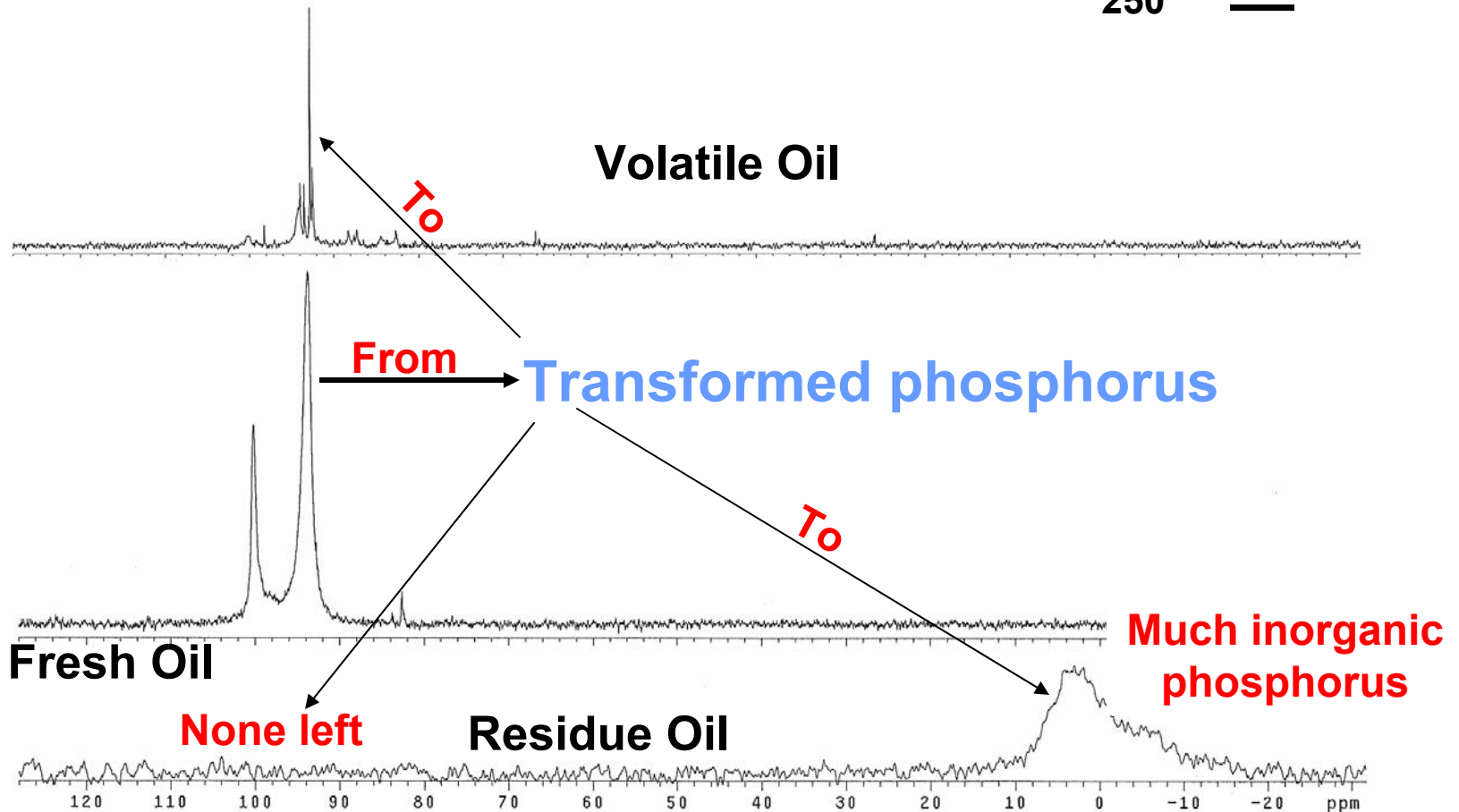
NMR analysis of Oil A @ 165°C

$$PEI_{165} = \underline{13}$$



PEI Values at Ring Belt and Lower Engine Operating Temperatures

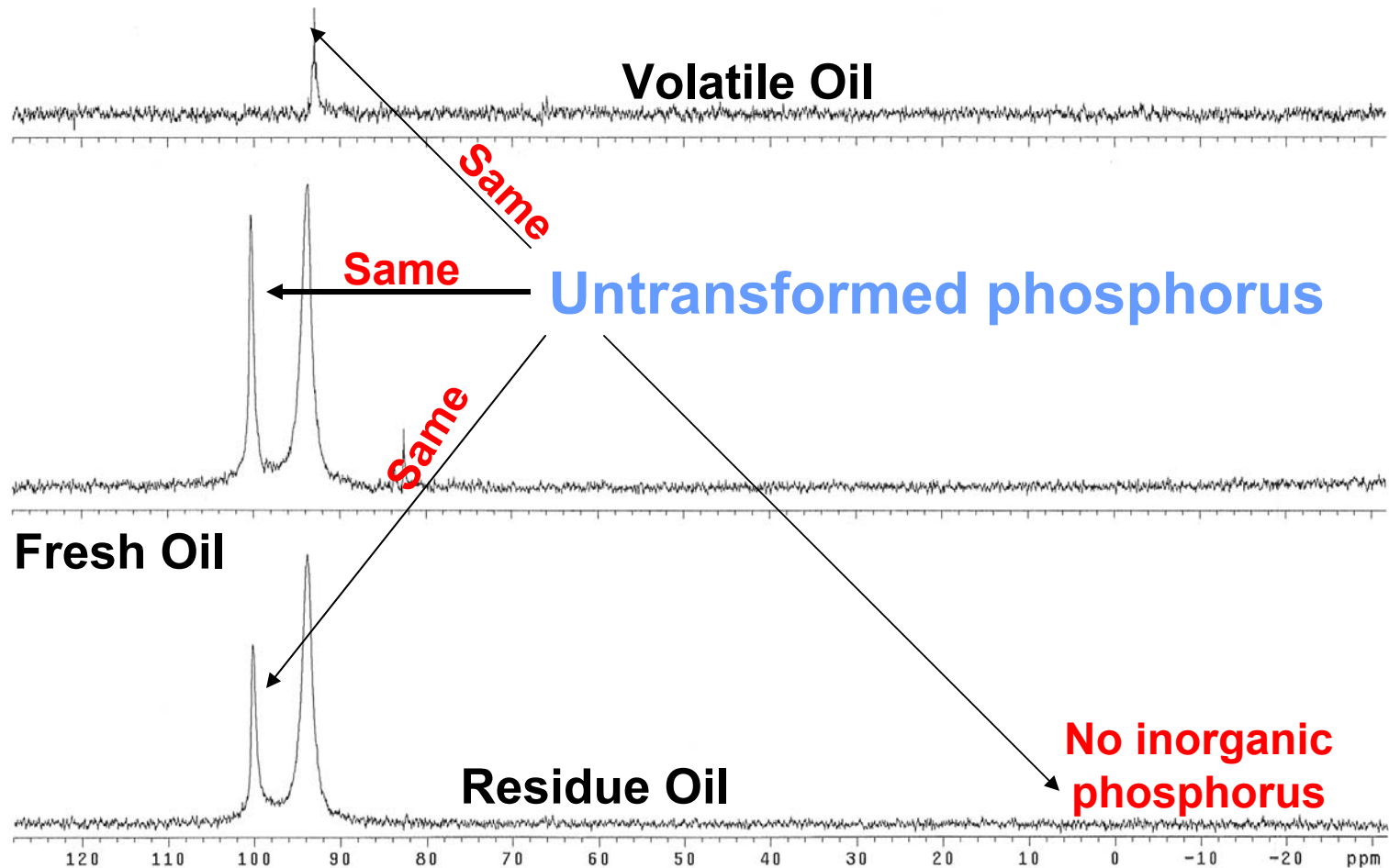
NMR analysis of Oil B @ 250°C
 $PEI_{250} = \underline{20}$



PEI Values at Ring Belt and Lower Engine Operating Temperatures

NMR analysis of Oil B @ 165°C

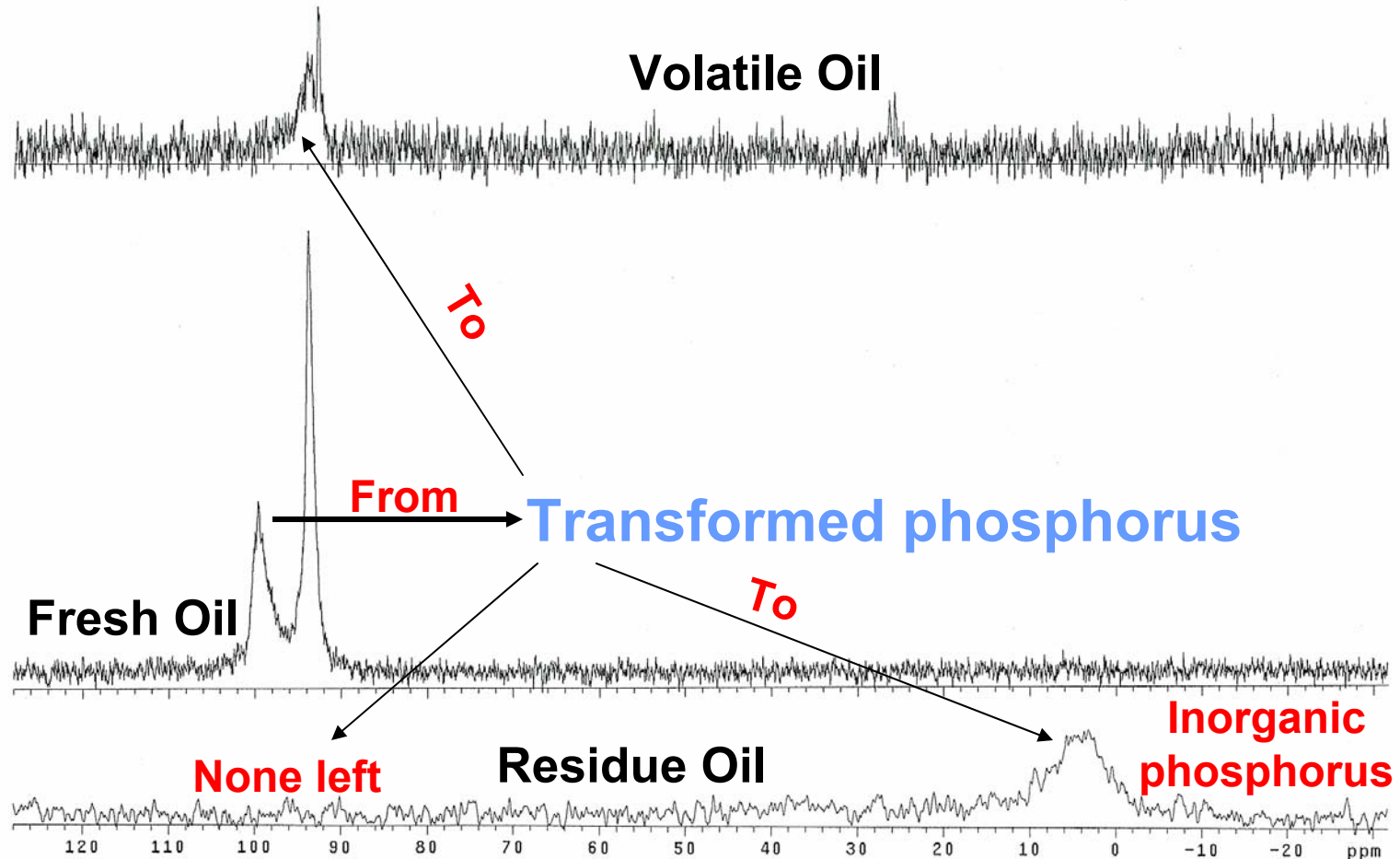
$$PEI_{165} = \underline{7}$$



PEI Values at Ring Belt and Lower Engine Operating Temperatures

NMR analysis of Oil C @ 250°C

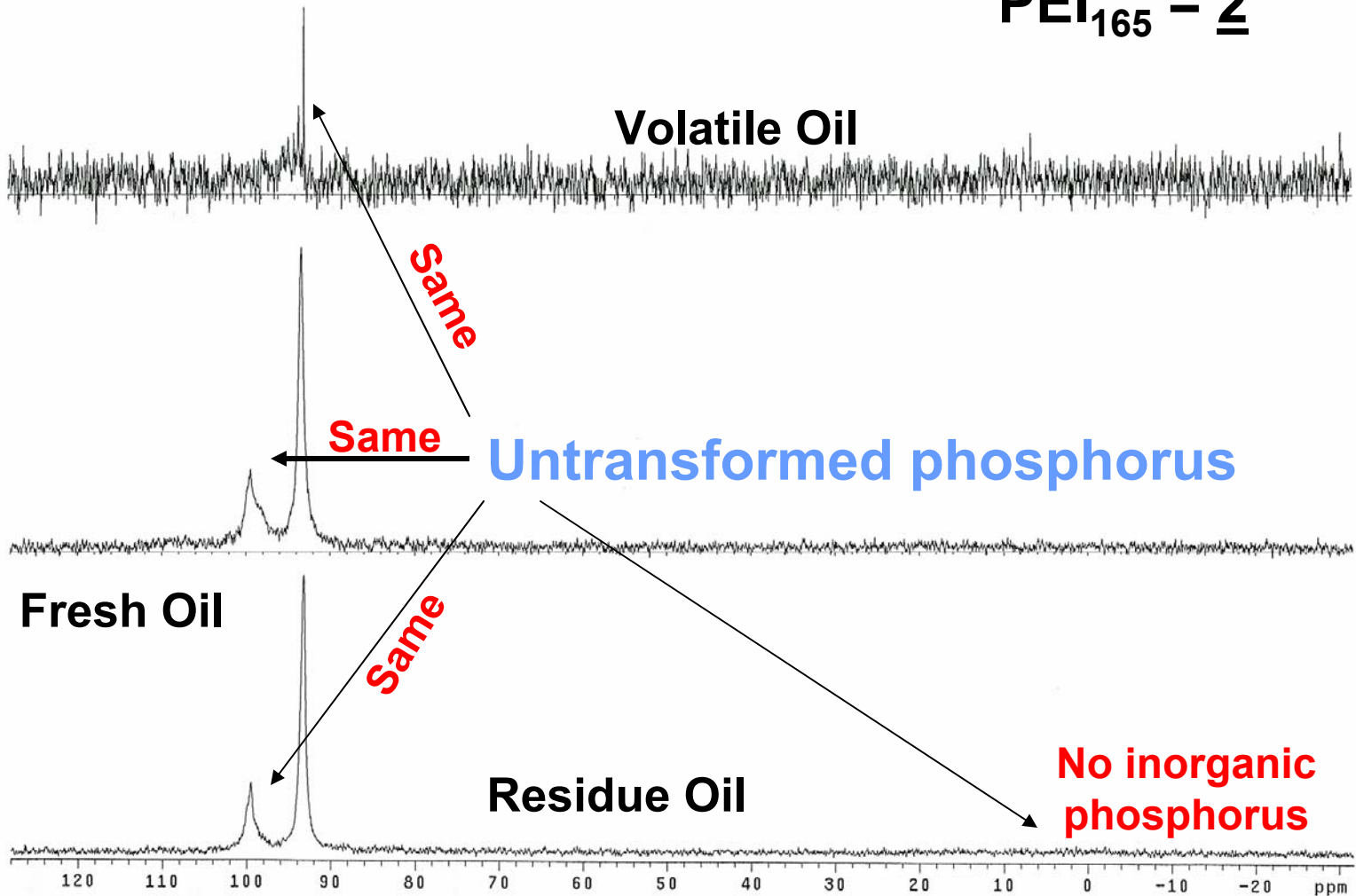
$$PEI_{250} = \underline{8}$$



PEI Values at Ring Belt and Lower Engine Operating Temperatures

NMR analysis of Oil C @ 165°C

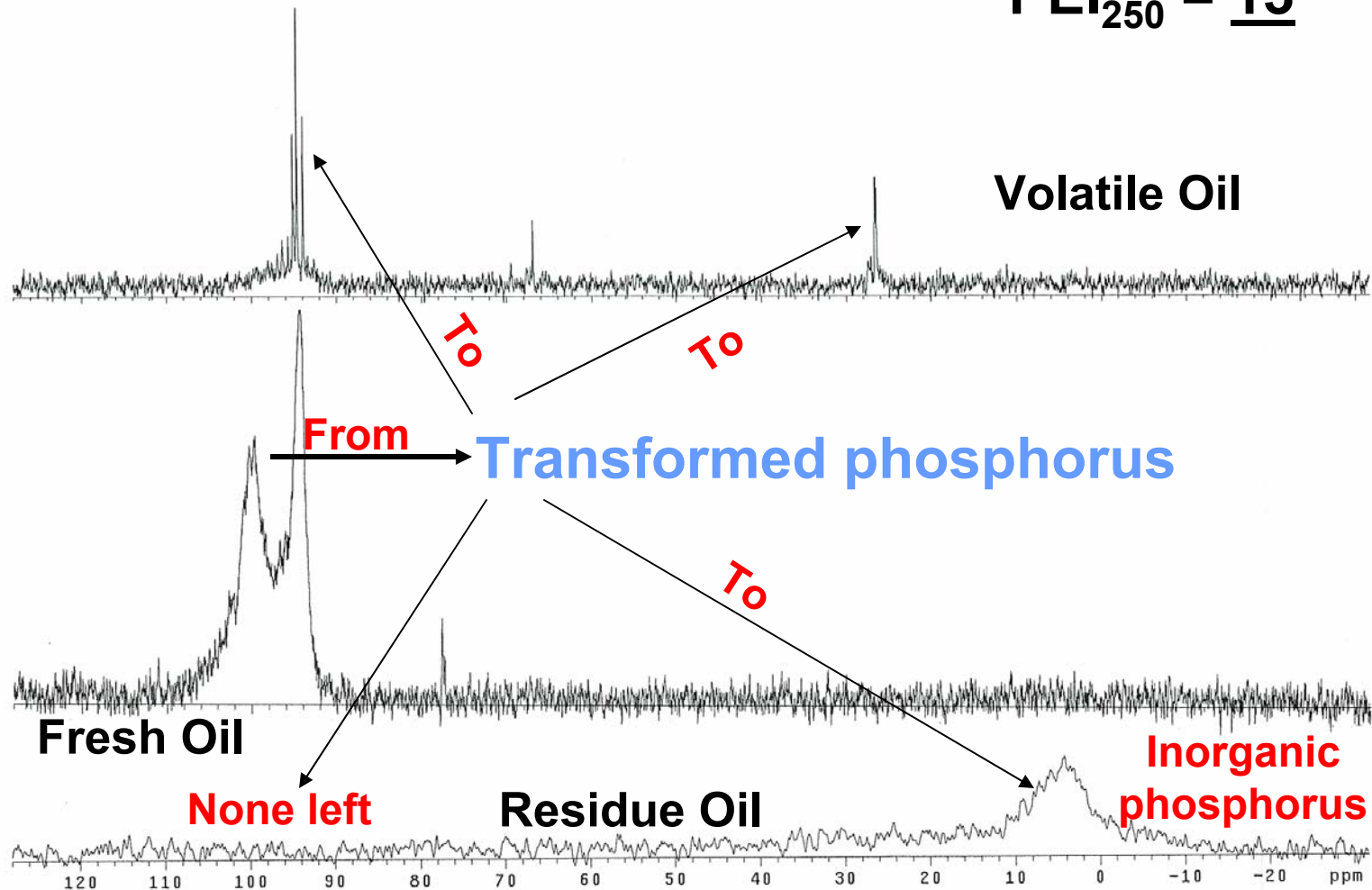
$$PEI_{165} = \underline{2}$$



PEI Values at Ring Belt and Lower Engine Operating Temperatures

NMR analysis of Oil D @ 250°C

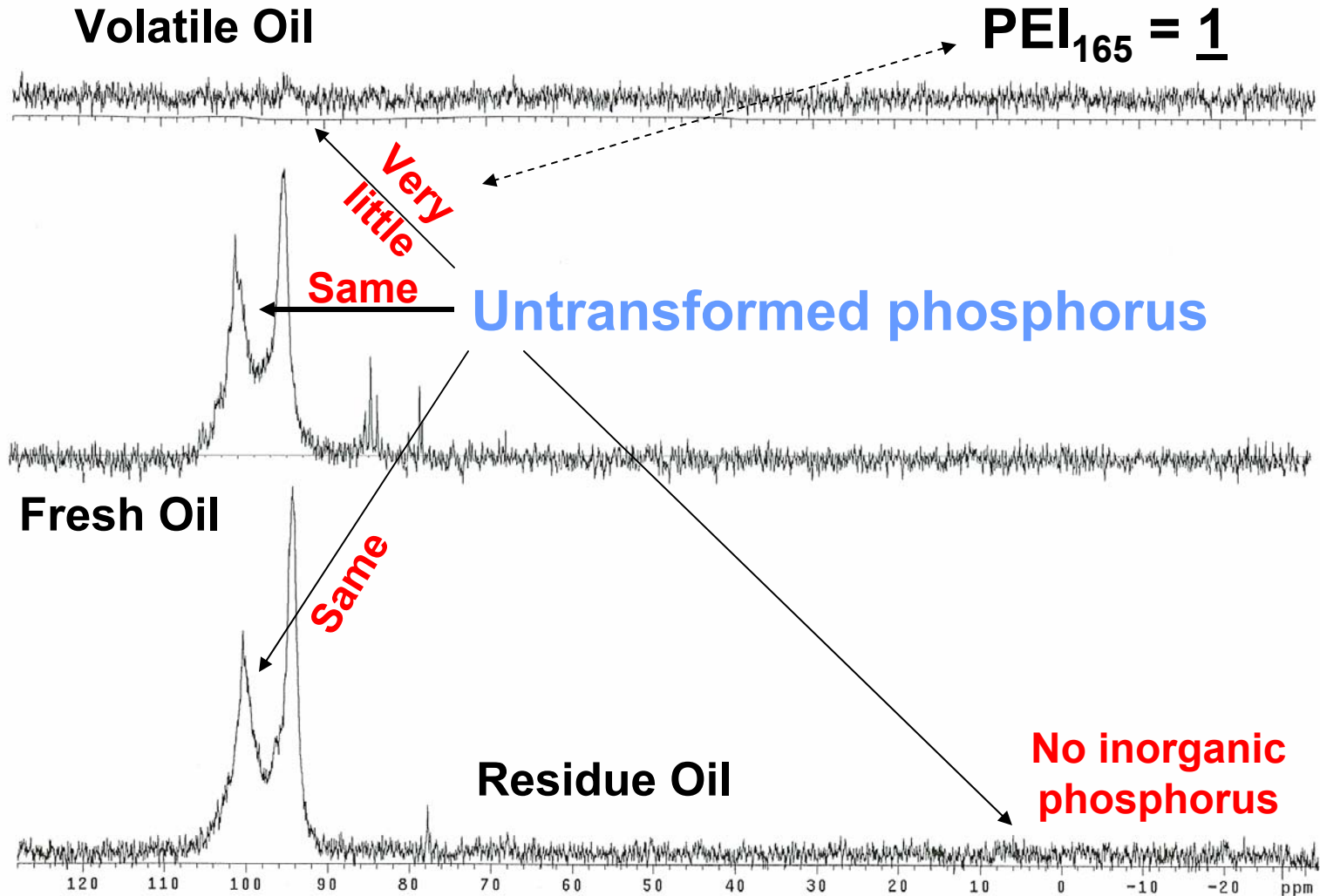
$PEI_{250} = \underline{13}$



PEI Values at Ring Belt and Lower Engine Operating Temperatures

NMR analysis of Oil D @ 165°C

$PEI_{165} = 1$



PEI Values at Ring Belt and Lower Engine Operating Temperatures

The data in these last few slides show that :

1. There is a marked change in the degree of susceptibility to decomposition among these four oils when the temperature of determining PEI is reduced.
2. The 165°C spectra show no formation of inorganic phosphates so evident in the NMR spectra at 250°C.
3. Interestingly, Oils B, C, and D show no significant change in the chemistry of their ZDDPs at 165°C
4. In contrast, Oil A shows molecular change in its ZDDP at 165°C but also indicates more resistance to form inorganic phosphates at 250°C.

Since Oils A, B, C, and D had relatively moderate levels of phosphorus volatility (shown by PEI_{250}), it was of interest to study engine oils from the North American market having high values of PEI_{250} and compare their PEI_{165} values.

PEI Values at Ring Belt and Lower Engine Operating Temperatures

Five engine oils were selected from the Institute of Materials (IOM) Engine Oil Database and, a small sample was requested and provided by IOM for analysis.

All of the oils were from North America.

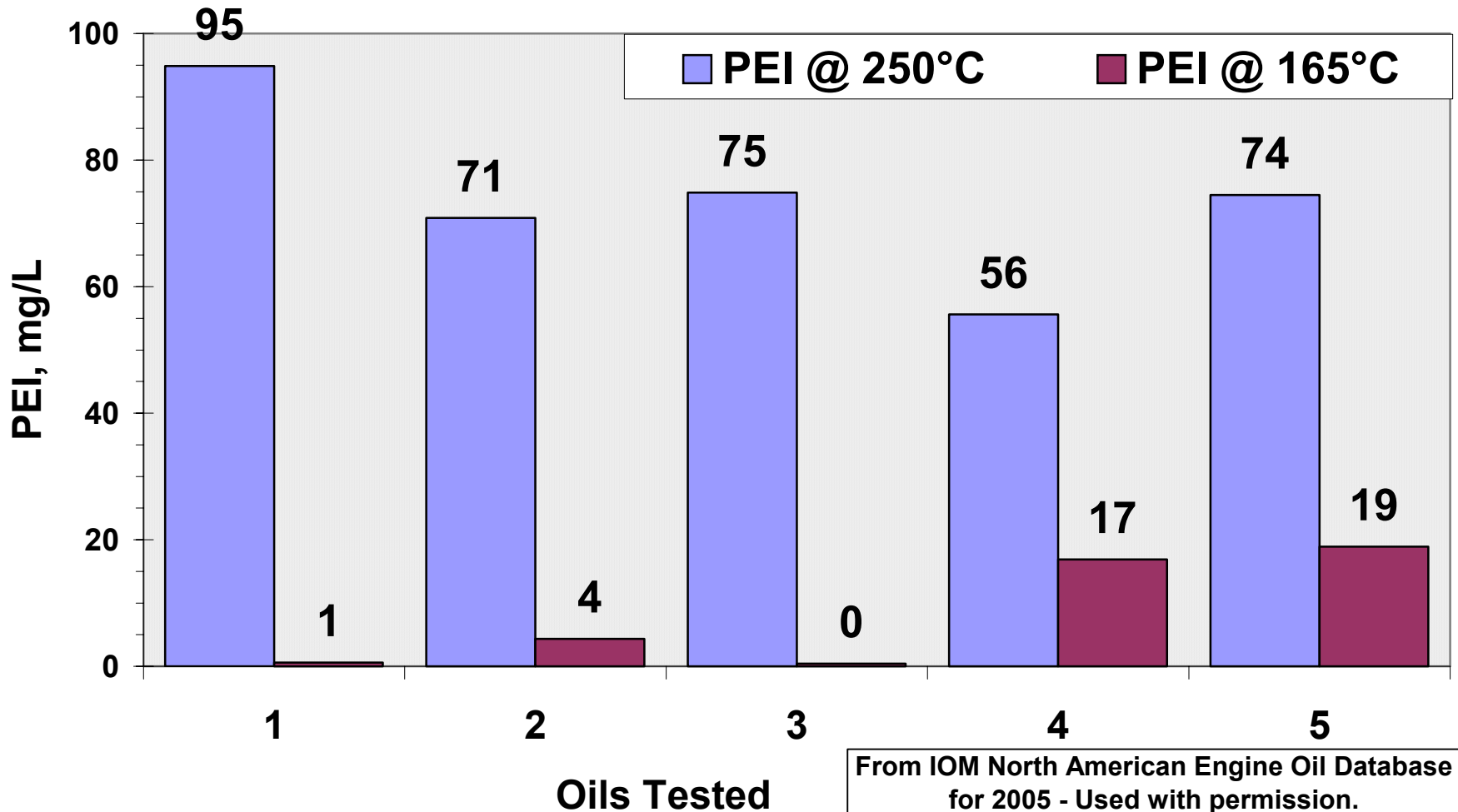
Phosphorus concentrations in the fresh oils ranged from 780 to 1520 PPM.

PEI₂₅₀ values ranged from 56 to 95 which placed all five among the 100th percentile of highest phosphorus volatility.

The following graph compares their PEI₁₆₅ and PEI₂₅₀ values.

PEI Values at Ring Belt and Lower Engine Operating Temperatures

Comparison of PEI₂₅₀ and PEI₁₆₅ Values of Engine Oils Having High PEI₂₅₀



PEI Values at Ring Belt and Lower Engine Operating Temperatures

The data in the last graph show that the difference between PEI_{165} and PEI_{250} can be very great and that phosphorus volatility of some engine oils may rise rapidly with increasing operating temperatures..

Although all five oils show considerable difference in phosphorus volatility between 165° and 250°C, Oils 1 and 3 are particularly susceptible to change.

This does not seem to be a function of initial concentrations of phosphorus since Oils 1 and 3 have reasonable initial phosphorus levels of 780 and 839 PPM, respectively.

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Summary::

The Phosphorus Emission Index can be measured at any one or any set of relevant engine oil operating temperatures.

NMR data on the fresh, volatilized, and residual oil from PEI tests at 250° and 165°C have shown the change in chemical responses of various ZDDPs.

PEI₁₆₅ studies on engine oils having very high values of PEI₂₅₀, indicates that large changes in phosphorus volatility will occur between these temperatures.

Such response of high PEI₂₅₀ oils is not a function of initial concentrations of phosphorus.

Study of the change of ZDDP response to temperature using the PEI_{temp} technique should give interesting information and help establish relevant engine oil responses.