Separation of Linear Alkanes from the UCM in Lube Oil and PM
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ABSTRACT The Carbon Preference Index (CPI) is used in assessing the relative contribution from anthropogenic and biogenic sources in particulate matter that is found in ambient air. The CPI is determined by calculating the ratio of the sum of odd- to the sum of even-carbon alkanes found in the soluble organic fraction of particulate matter samples. However, there are many cases where the CPI cannot be reliably calculated because GC/MS analysis of their linear alkanes is difficult. This arises from the similar nature of the non-polar compounds, i.e., linear and branched alkanes and cycloalkanes, found in these samples, which are difficult to resolve by gas chromatography. Typical chromatograms contain many overlapping peaks that produce a large hump commonly described as the unresolved complex mixture (UCM) interfering with the identification of alkanes. A project was initiated to therefore minimize or eliminate this UCM. The size and shape selective properties of molecular sieves were investigated to separate alkanes from the UCM. Result from tests using molecular sieves will be presented.

Several sieves were tested on pure alkanes and lube oils. Lube oils were used because it has been shown that they contribute to particulate matter in ambient air and contain many of the compounds that give rise to a large UCM. Data obtained with a 5Å pore size showed the most promising results and it was selected for further testing. Diluted mixtures of pure alkanes were exposed to the 5Å molecular sieves and resulted in a 95% uptake. It was also shown that the alkanes could be extracted (ca. 67%) from the sieve using a mixture of acid and hexane. Further tests with lube oil samples were done using deuterated alkanes as recovery surrogates. However, data from the experiments indicated that the extraction of the alkanes from the lube oil samples is more difficult. Modifying the extraction procedure using a sonicator bath has yielded a method where alkanes can be obtained in higher yields from lube oil samples with a significant reduction of the UCM.

Objectives

• Investigation of molecular sieves to develop a separation technique to improve GC/MS analysis of alkanes found in lube oil and particulate matter samples
• Correct identification of linear alkanes up to C38 to allow for improved calculation of the Carbon Preference Index (CPI)

n-ALKANE SEPARATION SCHEME

The drawing above shows the general scheme to remove alkanes from the UCM.
• The sample is exposed to the molecular sieve.
• The alkanes are loaded into the sieve and separated from the UCM.
• The alkanes are then removed from the sieve and analyzed.

SIEVES AND UREA ADDUCTION TESTS FOR ALKANE UPTAKE

TEST RESULTS

No alkanes were taken up by the sieve
• ~95% of the alkanes were taken up by the sieve
Alkanes and a portion of the UCM are taken up by the Urea

In light of these results the 5 Å sieve was selected for further investigation.

LOADING OF ALKANES IN THE MOLECULAR SIEVE (MS)

• ~2500:1 sieve to alkane ratio, Reflux in isooctane (25 ml, 98°C, ~6hrs), Filter

PRELIMINARY SEPARATION TEST WITH A 5 SIEVE

The figures show the mass/5 chromatograms of
a) Lube Oil spiked with alkanes
b) Same lube oil treated with MS
c) Pure alkane mixture
• The absence of alkanes in b) indicate that the alkanes have been taken up by the sieve
• Note the blue dotted lines indicating the shift in retention time between the pure alkanes and the alkanes in the lube oil

EXTRACTION OF ALKANES FROM A 5 SIEVE

Different methods were examined to remove the alkanes from the sieve:
• Accelerated Solvent Extractor:
  a) all trials resulted in low yields: ~2.5 – 38 %
  b) Soxhlet:
• all trials resulted in low yields: ~< 19 – 53 %
• Hydrolysis:
• most successful approach, optimized conditions: HCl (50 ml, 30%) + hexane (5 ml), ~6 hours stirring, 45–50°C (heating mantle)
  Extract with additional 2 X 5 ml hexane

Recovery % of Alkanes From Molecular Sieves

TRIALS ON LUBE OIL SAMPLES (with UCM)

• Deuterated alkanes (dC; 5 µg/ml) used to determine the efficiency of the method.
  (no interference with alkanes present in the sample)
• Method was less efficient to extract alkanes due to UCM (matrix effect)
• Method modified by using a sonicator bath to extract the alkanes
• Tests with lube oil dissolved in hexane or cyclohexane (1ml) to study solvent competition effect and influence on recoveries.

MODIFIED METHOD

• Loading of 1 sieve to lube, Reflux in isooctane (25 ml, 98°C, 6 hrs.), Filter
• Extraction
• HCl (50 ml, 30%) + hexane (5 ml)
• Sonication (4 Hrs.), 40-50°C (T˚ attained after sonication)
• Extract with additional 2 X 5 ml hexane

CONCLUSION

• A method was developed that reduces the effect of the UCM found in lube oil samples and allows for quantification of alkanes up to C38.
• The use of deuterated alkanes with a wide carbon distribution (C12-C36) as surrogates allow for better correction of the n-alkane recoveries.
• Similar recoveries of n-alkanes in hexane or cyclohexane were shown.
• Data show that hexane affects recovery of lighter alkanes and this is most likely due to the competition of hexane for the molecular sieve pores.