

Separation of Linear Alkanes from the UCM in Lube Oil and PM

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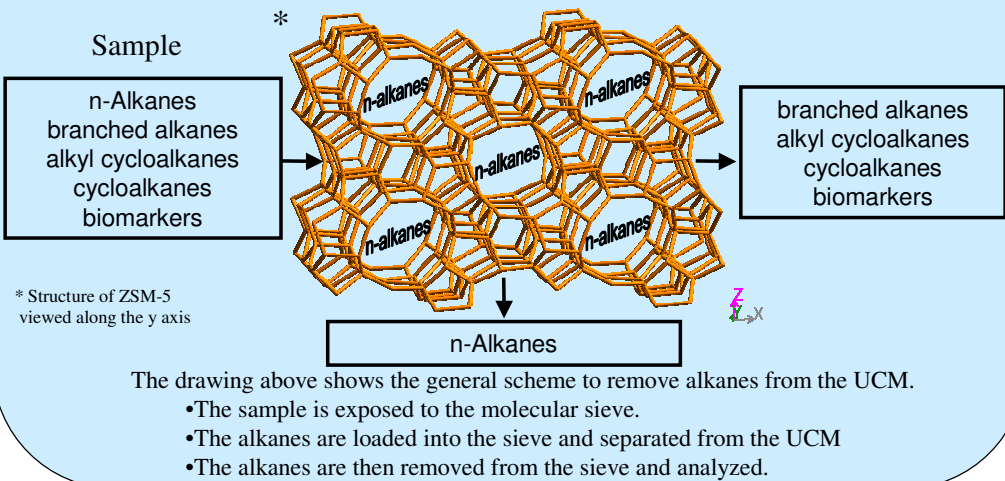
ABSTRACT The Carbon Preference Index (CPI) is used in assessing the relative contribution from anthropogenic and biogenic sources in particulate matter that is found in ambient air. The CPI is determined by calculating the ratio of the sum of odd- to the sum of even-carbon alkanes found in the soluble 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 sieve showed the most promising results and it was selected for further testing. Diluted mixtures of pure alkanes were exposed to the 5Å molecular sieve 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



SIEVES AND UREA ADDUCTION TESTS FOR ALKANE UPTAKE

TEST

4 Å molecular sieve :

5 Å molecular sieve :

Urea adduction (7Å Pore size) :

RESULTS

No alkanes were taken up by the sieve

~95% of the alkanes were taken up by the sieve

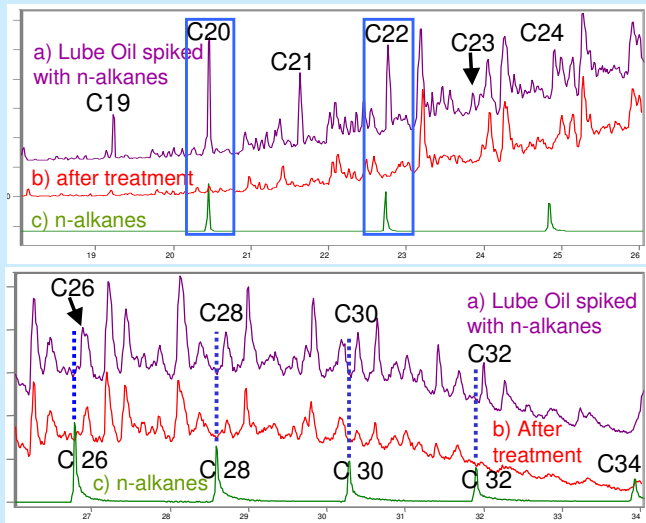
Alkanes and a portion of the UCM are taken up by the Urea

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 5 Å SIEVE



- The figures show the m/z 85 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 5 Å SIEVE

Different methods were examined to remove the alkanes from the sieve:

- Accelerated Solvent Extractor:**
- all trials resulted in low yields: ~2.5 – 38 %
- 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

Level: ug/ml	25	10	1
Carbon #	Average	Average	Average
C10	52	45	63
C12	51	55	80
C14	54	60	69
C16	58	64	74
C18	62	66	75
C20	67	67	85
C22	68	66	84
C24	66	64	89
C26	66	65	92
C28	66	64	89
C30	60	65	82
C32	59	63	76
C34	63	66	68
C36	58	65	62
C38	66	72	64
average	61	63	77

Avg. Std. Dev.: 25 ug/mL: 5; 10 ug/mL: 11; 1 ug/mL: 24

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 sieve**
- ~2500:1 sieve to alkane, 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

Recovery % of dC from Lube Oil With and Without Sonication

Carbon #	Without sonication 4 trials	With sonication 7 trials
dC12	25	50
dC16	18	45
dC20	22	49
dC24	25	53
dC30	29	60
dC36	28	58
Average	24	52

Recovery % of dC from Lube Oil Dissolved in Various Solvents

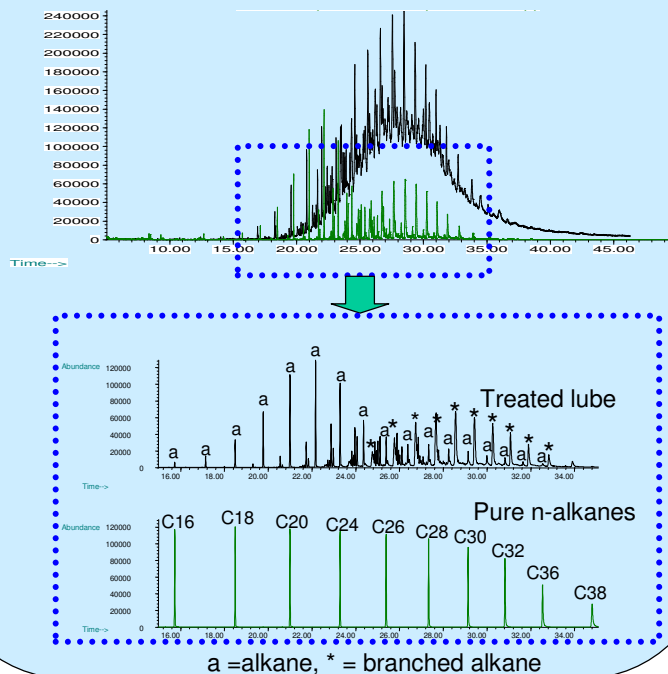
Carbon #	Lube in Cyclohexane 7 trials		Lube in Hexane 4 Trials	
	Average	Std. Dev.	Average	Std. Dev.
dC12	50	6	35	3
dC16	45	9	49	4
dC20	49	10	58	4
dC24	53	12	58	4
dC30	60	11	68	6
dC36	58	11	80	8
Average	52	10	58	5

Recovery % of dC and n-Alkanes in the Presence of Various Solvents

Carbon#	Cyclohexane (1 mL)		Hexane (1 ml)		No solvent added	
	Average	Adj. Rec.	Average	Adj. Rec.	Average	Adj. Rec.
C10	54	103	25	65	55	101
dC12	53		39		54	
C12	57	110	40	86	58	104
C14	52	101	46	99	58	105
C16	51	99	51	110	59	106
dC16	50		54		57	
C16	52	101	56	96	60	102
dC20	53	103	63		60	
C20	54	104	60	99	61	103
C22	55	107	60	98	62	104
dC24	53		59		60	
C24	54	88	59	93	63	101
C26	59	96	58	91	64	104
C28	65	106	62	98	68	110
dC30	70		68		64	
C30	64	92	63	89	64	99
C32	65	93	65	92	58	90
C34	63	90	66	94	55	84
dC36	70		73		66	
C36	64	92	68	93	58	88
C38	74	105	73	100	66	100
Average	59		57		60	

Avg. Std. Dev.: cyclohexane: 10; hexane: 10; No solvent: 12

Chromatograms of Lube Oil (m/z 85) (spiked with deuterated alkanes)



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.



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