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COMPARISON OF INTERLABORATORY MASS SPECTRAL HYDROCARBON TYPE DETERMINATIONS BY THE ROBINSON METHOD

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INTRODUCTION

Mass spectroscopy has been used by the petroleum industry to analyze petroleum product streams and fractions ever since the introduction of mass spectroscopy for chemical analysis in the early 1950's. The capability of mass spectroscopy to identify the various compound types in the complex petroleum mixtures has allowed refiners and process researchers to characterize more fully their commercial products or to follow the changes in the reaction products of processes. Several mass spectroscopic methods (1) have been standardized by the American Society for Testing and Materials (ASTM). These methods cover the analysis of hydrocarbon types in low olefinic gasoline (D-2789), hydrocarbon types in middle distillates (D-2425), hydrocarbon type analysis of gas-oil saturate fractions (D-2786) and aromatic type analysis of gas-oil aromatic fractions (D-3239). These methods were standardized in the mid-1960's based on research in the industry using the ubiquitous CEC Model 21-103 mass spectrometer.

The detailed type analysis for petroleum mixtures more complex than naphthas required prior chromatographic separation into aromatic and non-aromatic fractions in order to resolve mutual interferences between the higher order cycloparaffins and the aromatics. This is normally performed using ASTM Method D-2549 for Separation of Representative Aromatic and Nonaromatic Fractions of High-Boiling Oils by Elution Chromatography. The aromatics and non-aromatics or saturate fractions are then analyzed separately.

In 1971 Robinson (2) published a detailed method that resolved up to 4 saturate and 21 aromatic compound types in distillates and gas oils boiling in the 100-600°C range without physical separation of the sample. The method used a base-line technique to resolve the total mass spectra into separate saturates and aromatics spectra and from each spectrum to determine the concentrations of each of the 25 types in the total sample. The advantages of this new method were obvious: a one-step analysis with significant savings in time and costs and also applicable to the full volatility range of petroleum products. With the ready availability of the computer code from Robinson himself the industry soon adopted and put to general use the Robinson method.

The Robinson and ASTM methods were developed using a more or less standardized instrument, the CEC Model 21, and are dependant upon the response factors used and inherent in the calculation procedures of the methods and especially in the Robinson method matrices. The response factors are of course a function of the ionization pattern of the mass spectrometer source. This ionization pattern can and does change among spectrometers. A calibration method is standardized on n-hexadecane and adjustment of the source for constant response ratios between different ion sums should assure comparability between sources.

Most magnetic-deflection type mass spectrometers respond similarly to the CEC spectrometer and the methods have been found to apply well using these. The magnetic sector instruments, however, are expensive and complex when compared with the more recently introduced low-resolution quadrupole mass spectrometers. The possibility of applying these methods to the lower cost quadrupole spectrometers thus arises. The ionization pattern of the latter is, however, different from that of the magnetic sector instrument and if the methods are to operate successfully the quadrupole analyzer must be made to emulate as closely as possible the magnetic sector instrument.

A further incentive to attempt the application of the Robinson method to the quadrupole spectrometers is the increasing availability of these concurrent with the decrease in cost, increased portability and simpler and less costly data systems based on personal computers. A magnetic-sector system equivalent to the old CEC which today costs about \$500,000 could be replaced by a quadrupole system for about \$100,000. The relatively low cost and ease of operation of the quadrupole system could provide a powerful analytical tool for many researchers in the petroleum industry and eventually for process operators.

The CANMET Energy Research Laboratories therefore undertook in 1984 to support contract work to investigate and develop application of the Robinson method for use on the Finnigan 4500 quadrupole mass spectrometer system (3). The contract was awarded to Zenon Environmental Inc. of Burlington, Ontario at a total cost of \$118,593. The contractor modified the Robinson method software to operate on the Finnigan system, developed and tested a standardized calibration and analysis procedure, and finally tested the method using standards previously analyzed by the Robinson method on a magnetic sector instrument. The contractor, however, was not able to duplicate satisfactorily the results of the magnetic sector instrument. There were significant differences in most hydrocarbon types reported for all samples. However CANMET was able to duplicate successfully the magnetic sector results using its Finnigan 4500. The initial failure was probably caused by inadequate adjustment of the Finnigan source by the contractor. It is essential that the Finnigan instrument be carefully tuned to manufacturer's specifications.

This paper reports the results of the interlaboratory study conducted at CANMET/ERL with the cooperation of two industrial petroleum research laboratories to verify the applicability of the Robinson method to the Finnigan 4500.

INTERLABORATORY TESTING

A set of five samples was obtained for testing by three laboratories to compare the performance of the different spectrometers when using the Robinson method: Petro-Canada Sheridan Park Research Laboratory, Imperial Oil Limited Sarnia Research Laboratory (ESSO) and the CANMET Energy Research

Laboratories.

The spectrometers used by each laboratory are described below. Petro-Canada used a CEC magnetic sector spectrometer; Imperial Oil used a Hewlett-Packard quadrupole mass detector equipped with a Brunfeldt batch inlet; ERL used a Finnigan 4500 quadrupole mass spectrometer with a gas chromatography inlet system.

The samples included middle distillates from conventional petroleum sources and from oil sand synthetic crudes. The samples were also selected to represent the full range of aromaticity found in middle distillate petroleum products. In addition a few gas oils were tested to explore the higher volatility limit of the method. The samples are described in Table 1.

DISCUSSION OF INTERLABORATORY RESULTS

Tables 2 to 6 give the results of the analyses by the Robinson method for each of the five samples. The results show that the three laboratories differ slightly for each sample but overall the results are similar. The comparisons are better seen in the bar charts given for each component in Figures 1 to 8, which are discussed individually in the following paragraphs.

SATURATES (Fig. 1)

The overall saturate levels are comparable with the possible exception of sample ARL-6. CANMET results show a significantly greater saturate level than the other two laboratories. Generally results for the other four samples are within 5%, however CANMET results are slightly higher than the other two. For ARL-6 CANMET's levels are 15-20% higher. Sample ARL-6 is a heavy gas oil with a significantly higher boiling point distribution than the other four samples. More than 50% of the sample boils above 325°C while more than 10% boils above 400°C.

Preliminary tests using CANMET's Finnigan gas chromatography system indicated that compounds with boiling points greater than 400°C are not totally injected into the spectrometer source but are trapped in a cold spot between the column and the mass spectrometer detector. This is shown to be the cause if the ARL-6 results are examined in detail. The CANMET results show a lesser proportion of the compounds with Z numbers less than -12; these are the high molecular weight compounds with the higher boiling points.

PARAFFINS AND CYCLOPARAFFINS

Figures 2 to 5 compare the individual results for the different saturate components. Overall the comparison is good for all the paraffins and the mono- and di-cycloparaffins. However, substantial variations among the laboratories can be seen in the case of the 3-ring cycloparaffins. This may again be

caused by the different response of the inlet systems to high boiling compounds. The multi-ring condensed cycloparaffins are the waxy high melting and high boiling compounds found in crude oils.

AROMATICS (Fig. 6)

The response of the different spectrometers to the aromatic compounds also shows some variations. Except sample ARL-6, the total aromatics are reasonably close however, CANMET's results are generally lower than the other two laboratories. Individual aromatics show more variations and the CANMET results show a greater departure from those of the other two laboratories. This may be explained in part by the loss of the high boiling polynuclear compounds in the Finnigan gas chromatograph inlet. ✓

CONCLUSIONS

The Finnigan 4500 GC/MS System can be set up to provide hydrocarbon type analysis by the Robinson method with a good degree of comparability with the classical mass spectroscopic systems for which the method was developed. The system set-up procedures have been described and proven on the CANMET Finnigan 4500 System. However, results obtained however should be qualified according to the following conditions:

- (a) the Finnigan system, unless suitably modified, cannot handle samples with fractions boiling much higher than 400°C. ✓
- (b) for more accuracy, samples to be compared should be run as a series within a relatively short time span to ensure the instrument conditions are constant. Conditions may change between set-up procedures.
- (c) relative bias between laboratories would be of the order of 10% of the measured levels. Further multiple tests and a statistically acceptable interlaboratory testing program would have to be carried out to determine the precision and bias of the different instruments. ✓

ACKNOWLEDGEMENTS

Appreciation is due to Mr. John Coburn and colleagues of Zenon Environmental Inc. who developed the Robinson method software for the Finnigan 4500 system under contract to the Department of Energy, Mines and Resources.

Special appreciation is expressed to Dr. Ian Fisher of Petro-Canada's Research Centre in Sheridan Park and to Dr. Terry Ashe of Imperial Oil Limited's Sarnia Research Centre who readily collaborated with CANMET in this interlaboratory test. Appreciation is further extended to Zenon Environmental Inc.

REFERENCES

1. ASTM, "Annual Book of ASTM Standards, Section 5, Petroleum Products, Lubricants, and Fossil Fuels", Vol. 05.02 (1987).
2. Robinson, C.J. "Low-resolution mass spectrometric determination of aromatics and saturates in petroleum fractions", Anal Chem, 43;1425, 1971.
3. Zenon Environmental Inc. "Development of a rapid GC/MS method for the type characterization of petroleum hydrocarbons using a Finnigan 4500 GC/MS" Final Report prepared for Energy, Mines and Resources Canada under Supply and Services Canada Contract No. OSQ84-00267, March 1987.

Table 1 - Properties of test samples

Sample	Type	Density	Aromatics NMR C-13 %	Distillation, %				
				IBP	10	50	90	FBP
ARL-1	Mid dist. cut from Suncor syncrude	0.836	9.8	142	181	232	283	333
ARL-4	Light cycle oil	0.953	46.3	140	208	285	382	441
ARL-6	Heavy gas oil	0.912	14.9	152	231	327	408	482
ARL-9	No. 2 fuel oil	0.846	--	141	188	274	344	436
ARL-11	Fully hydrogenated Sample ARL-1	--	0.5	--	--	--	--	--

Table 2 - Sample ARL-1, Suncor synthetic crude middle distillate cut

Hydrocarbon types	Z No.	CANMET		Petro-Canada		Esso	
		Wt. %		Wt. %		Wt. %	
Saturates		77.9		75.3		74.1	
Paraffins	2		28.1		26.4		19.6
Cycloparaffins		49.7		48.9		54.5	
NonCond. Cycloparaffins	0		29.9		24.5		24.8
Cond. Cyclopara 2-Ring	-2		16.9		16.8		19.1
Cond. Cyclopara 3-Ring+	-4		2.9		7.6		10.6
Aromatics		22.0		24.8		25.8	
Monoaromatics		19.7		22.6		23.1	
Alkylbenzenes	-6		11.4		11.3		10.8
Naphthenebenzenes	-8		6.6		8.7		9.0
Dinaphthenebenzenes	-10		1.6		2.6		3.3
Diaromatics		2.1		2.2		2.7	
Naphthalenes	-12		1.0		1.6		1.7
Acenaphthenes,Dbzfurans	-14		0.0		0.1		0.4
Fluorenes	-16		1.0		0.5		0.6
Triaromatics		0.0		0.0		0.0	
Phenanthrenes	-18		0.0		0.0		0.0
Naphthenephenanthrenes	-20		0.0		0.0		0.0
Tetraaromatics		0.0		0.0		0.0	
Pyrenes	-22		0.0		0.0		0.0
Chrysenes	-24		0.0		0.0		0.0
Pentaaromatics		0.0		0.0		0.0	
Perylenes	-28		0.0		0.0		0.0
Dibenzanthracenes	-30		0.0		0.0		0.0
Aromatic Sulphur		0.0		0.0		0.0	
Benzothiophenes	-10S		0.0		0.0		0.0
Dibenzothiophenes	-16S		0.0		0.0		0.0
Naphthobenzothiophenes	-22S		0.0		0.0		0.0
Unidentified		0.0		0.0		0.0	
Class I with Naphphenan					0.0		0.0
Class II			0.0		0.0		0.0
Class III			0.0		0.0		0.0
Class IV			0.0		0.0		0.0
Class V			0.0		0.0		0.0
Class VI			0.0		0.0		0.0
Class VII			0.0		0.0		0.0

Table 3 - Sample ARL-4, Light cycle oil

Hydrocarbon type	Z No.	CANMET		Petro-Canada		Esso	
		Wt. %		Wt. %		Wt. %	
Saturates		29.6		24.5		28.7	
Paraffins	2		14.0		14.6		14.4
Cycloparaffins		15.6		9.9		14.3	
NonCond. Cycloparaffins	0		11.5		6.0		9.3
Cond. Cyclopara 2-Ring	-2		2.9		2.5		4.7
Cond. Cyclopara 3-Ring+	-4		1.2		1.4		0.3
Aromatics		68.4		75.4		71.2	
Monoaromatics		24.7		26.3		22.7	
Alkylbenzenes	-6		14.5		12.3		10.6
Naphthalenebenzenes	-8		10.2		11.6		9.9
Dinaphthalenebenzenes	-10		0.0		2.4		2.2
Diaromatics		34.5		33.6		30.9	
Naphthalenes	-12		24.6		22.4		19.8
Acenaphthenes, Dbzfurans	-14		4.3		6.2		6.0
Fluorenes	-16		5.6		5.0		5.1
Triaromatics		6.2		8.3		8.9	
Phenanthrenes	-18		5.9		7.6		7.7
Naphthenephenanthrenes	-20		0.3		0.7		1.2
Tetraaromatics		0.5		2.2		3.0	
Pyrenes	-22		0.1		2.0		2.5
Chrysenes	-24		0.4		0.2		0.5
Pentaaromatics		0.3		0.0		0.0	
Perylenes	-28		0.3		0.0		0.0
Dibenzanthracenes	-30		0.0		0.0		0.0
Aromatic Sulphur		2.2		5.0		5.7	
Benzothiophenes	-10S		0.7		1.9		2.2
Dibenzothiophenes	-16S		1.2		3.1		3.3
Naphthobenzothiophenes	-22S		0.3		0.0		0.2
Unidentified		1.1		0.0		0.0	
Class I with Naphphenan					0.0		0.0
Class II			0.4		0.0		0.0
Class III			0.1		0.0		0.0
Class IV			0.0		0.0		0.0
Class V			0.1		0.0		0.0
Class VI			0.0		0.0		0.0
Class VII			0.5		0.0		0.0

Table 4 - Sample ARL-6, Heavy gas oil

Hydrocarbon types	Z NO.	CANMET		Petro-Canada		Esso	
		Wt. %		Wt. %		Wt. %	
Saturates		78.8		62.8		57.3	
Paraffins	2		9.7		5.9		3.3
Cycloparaffins		68.9		56.9		54.1	
NonCond. Cycloparaffins	0		28.0		24.1		18.2
Cond. Cyclopara 2-Ring	-2		26.2		17.4		15.5
Cond. Cyclopara 3-Ring+	-4		14.7		15.4		20.4
Aromatics		21.1		37.2		42.7	
Monoaromatics		12.3		19.1		17.8	
Alkylbenzenes	-6		3.4		5.3		4.0
Naphthenebenzenes	-8		4.7		7.2		6.8
Dinaphthenebenzenes	-10		4.0		6.6		6.9
Diaromatics		5.3		10.3		13.3	
Naphthalenes	-12		2.8		4.0		4.0
Acenaphthenes,Dbzfurans	-14		0.9		3.0		4.6
Fluorenes	-16		1.5		3.3		4.7
Triaromatics		0.7		2.1		3.2	
Phenanthrenes	-18		0.7		1.5		1.8
Naphthenephenanthrenes	-20		0.0		0.6		1.4
Tetraaromatics		0.1		1.1		2.2	
Pyrenes	-22		0.1		1.0		1.7
Chrysenes	-24		0.0		0.1		0.5
Pentaaromatics		0.2		0.1		0.0	
Perylenes	-28		0.2		0.1		0.0
Dibenzanthracenes	-30		0.0		0.0		0.0
Aromatic Sulphur		2.2		4.5		5.9	
Benzothiophenes	-10S		1.9		2.6		3.5
Dibenzothiophenes	-16S		0.0		1.8		2.3
Naphthobenzothiophenes	-22S		0.2		0.1		0.0
Unidentified		0.1		0.0		0.1	
Class I with Naphphenan					0.0		0.0
Class II			0.0		0.0		0.0
Class III			0.0		0.0		0.1
Class IV			0.0		0.0		0.0
Class V			0.0		0.0		0.0
Class VI			0.0		0.0		0.0
Class VII			0.0		0.0		0.0

Table 5 - Sample ARL-9, No.2 Fuel oil

Hydrocarbon types	Z NO.	CANMET		Petro-Canada		Esso	
		Wt. %		Wt. %		Wt. %	
Saturates		76.0		71.6		72.5	
Paraffins	2		33.2		34.7		27.7
Cycloparaffins		42.7		37.0		44.8	
NonCond. Cycloparaffins	0		26.0		21.6		25.0
Cond. Cyclopara 2-Ring	-2		12.6		11.8		12.9
Cond. Cyclopara 3-Ring+	-4		4.1		3.5		6.9
Aromatics		23.9		28.4		27.4	
Monoaromatics		15.9		19.1		17.1	
Alkylbenzenes	-6		9.5		11.1		8.6
Naphthenebenzenes	-8		3.7		5.5		5.6
Dinaphthenebenzenes	-10		2.6		2.5		2.9
Diaromatics		6.4		8.1		8.6	
Naphthalenes	-12		4.3		6.1		6.1
Acenaphthenes, Dbzfurans	-14		0.8		1.3		1.5
Fluorenes	-16		1.1		0.7		1.0
Triaromatics		1.2		1.1		1.0	
Phenanthrenes	-18		1.0		1.0		1.0
Naphthenephenanthrenes	-20		0.1		0.0		0.0
Tetraaromatics		0.0		0.1		0.2	
Pyrenes	-22		0.0		0.1		0.2
Chrysenes	-24		0.0		0.1		0.0
Pentaaromatics		0.0		0.0		0.0	
Perylenes	-28		0.0		0.0		0.0
Dibenzanthracenes	-30		0.0		0.0		0.0
Aromatic Sulphur		0.1		0.1		0.5	
Benzothiophenes	-10S		0.0		0.1		0.5
Dibenzothiophenes	-16S		0.0		0.0		0.0
Naphthobenzothiophenes	-22S		0.0		0.0		0.0
Unidentified		0.2		0.0		0.0	
Class I with Naphphenan					0.0		0.0
Class II			0.1		0.0		0.0
Class III			0.0		0.0		0.0
Class IV			0.0		0.0		0.0
Class V			0.0		0.0		0.0
Class VI			0.0		0.0		0.0
Class VII			0.0		0.0		0.0

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11
1

Table 6 - Sample ARL-11, Fully hydrogenated ARL-1

Hydrocarbon types	Z No.	CANMET		Petro-Canada		Esso	
		Wt. %		Wt. %		Wt. %	
Saturates		95.7		96.5		97.2	
Paraffins	2		14.1		16.9		11.4
Cycloparaffins		81.4		79.6		85.8	
NonCond. Cycloparaffins	0		38.5		35.2		35.4
Cond. Cyclopara 2-Ring	-2		32.8		29.5		31.6
Cond. Cyclopara 3-Ring+	-4		10.1		14.9		18.8
Aromatics		4.2		3.5		2.8	
Monoaromatics		2.1		1.1		1.3	
Alkylbenzenes	-6		0.0		0.0		0.0
Naphthenebenzenes	-8		0.1		0.0		0.1
Dinaphthenebenzenes	-10		2.0		1.1		1.2
Diaromatics		1.3		1.3		1.3	
Naphthalenes	-12		0.0		0.4		0.2
Acenaphthenes, Dbzfurans	-14		0.0		0.0		0.0
Fluorenes	-16		1.3		0.9		1.1
Triaromatics		0.0		0.5		0.2	
Phenanthrenes	-18		0.0		0.5		0.2
Naphthenephenanthrenes	-20		0.0		0.0		0.0
Tetraaromatics		0.6		0.6		0.0	
Pyrenes	-22		0.4		0.6		0.0
Chrysenes	-24		0.2		0.0		0.0
Pentaaromatics		0.0		0.0		0.0	
Perylenes	-28		0.0		0.0		0.0
Dibenzanthracenes	-30		0.0		0.0		0.0
Aromatic Sulphur		0.0		0.0		0.0	
Benzothiophenes	-10S		0.0		0.0		0.0
Dibenzothiophenes	-16S		0.0		0.0		0.0
Naphthobenzothiophenes	-22S		0.0		0.0		0.0
Unidentified		0.0		0.0		0.0	
Class I with Naphphenan					0.0		0.0
Class II			0.0		0.0		0.0
Class III			0.0		0.0		0.0
Class IV			0.0		0.0		0.0
Class V			0.0		0.0		0.0
Class VI			0.0		0.0		0.0
Class VII			0.0		0.0		0.0

Figure 1
Comparison of saturate levels
determined by using the Robinson method

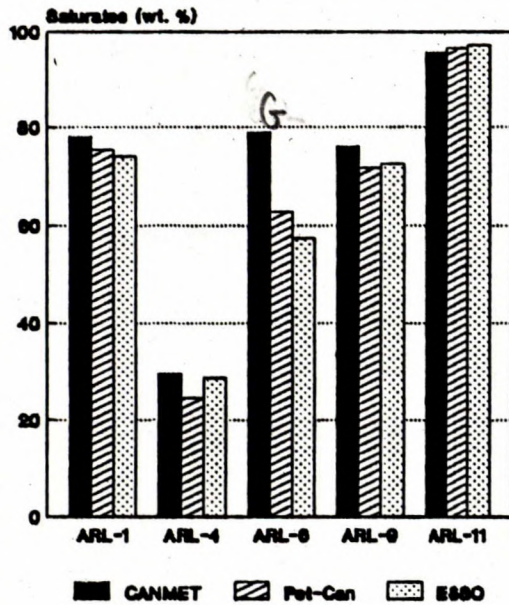


Figure 2
Comparison of paraffin levels determined
by using the Robinson method

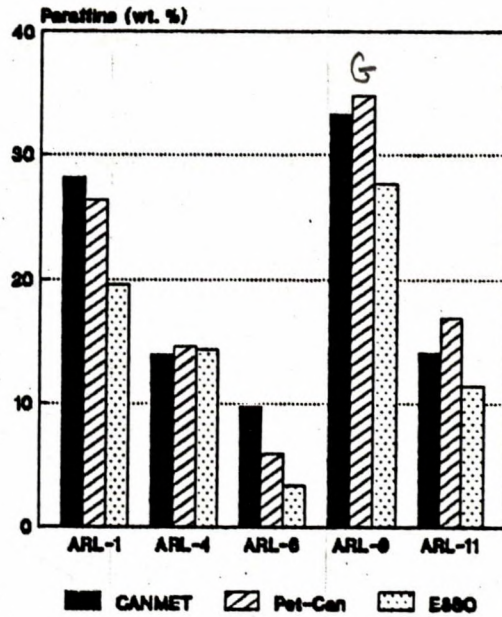


Figure 3
Comparison of monocycloparaffin levels
determined by using the Robinson method

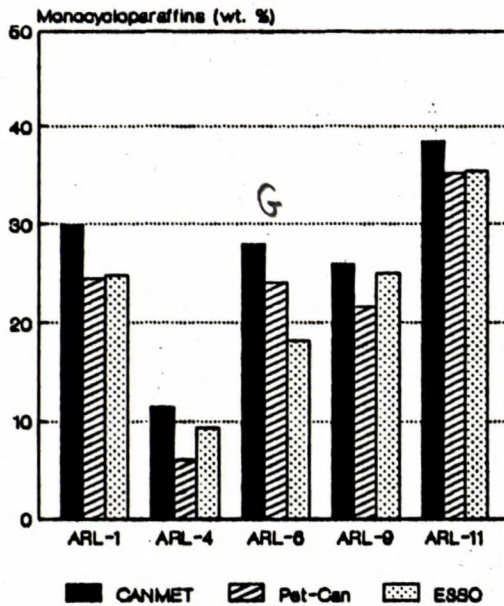


Figure 4
Comparison of dicycloparaffin levels
determined by using the Robinson method

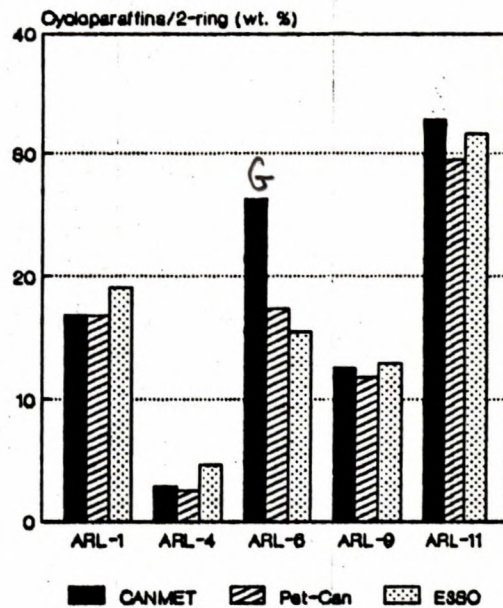


Figure 5
Comparison of triacyloparaffin levels
determined by using the Robinson method

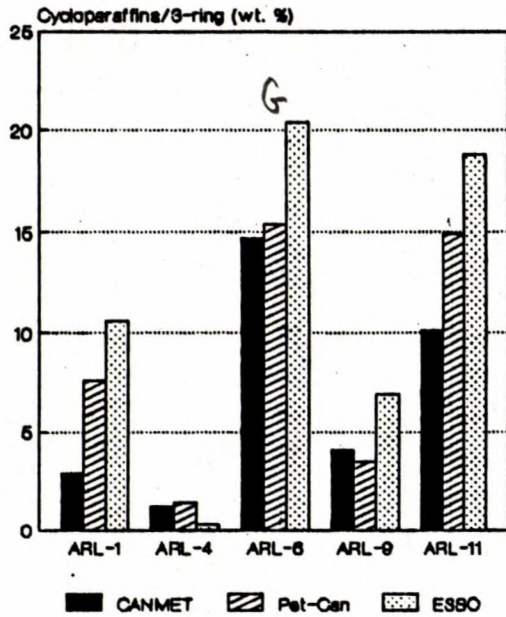


Figure 6
Comparison of aromatic levels
determined by using the Robinson method

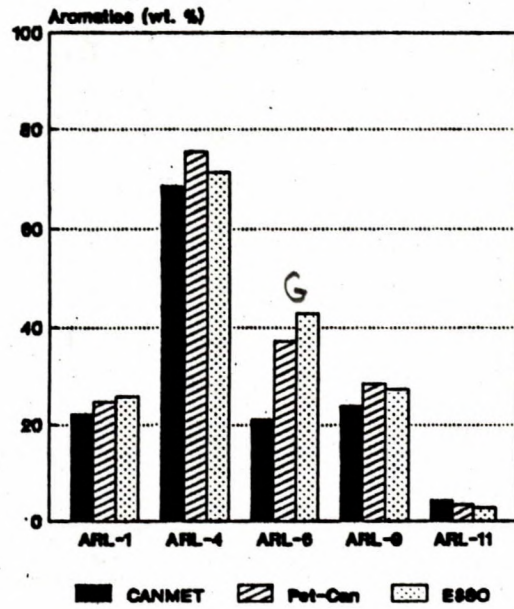


Figure 7
Comparison of alkylbenzene levels
determined by using the Robinson method

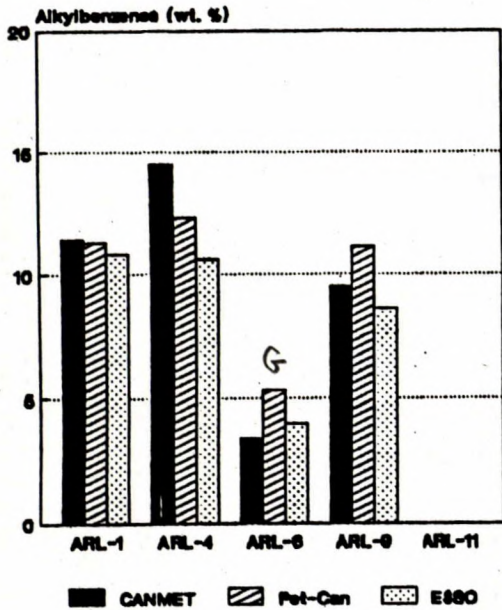


Figure 8
Comparison of naphthenebenzene levels
determined by using the Robinson method

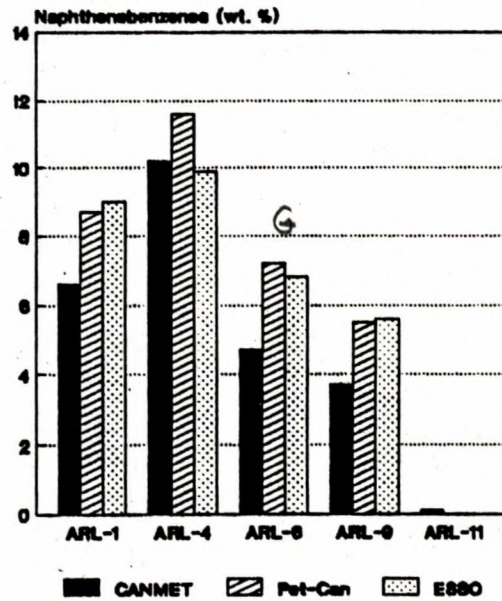


Figure 9
Comparison of dinaphthenebenzene levels
determined by using the Robinson method

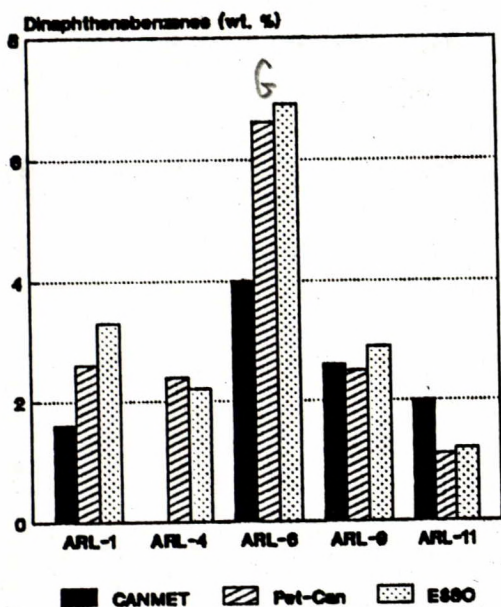


Figure 10
Comparison of naphthalene levels
determined by using the Robinson method

