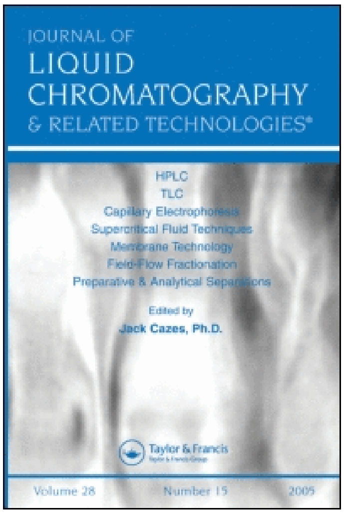

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Initial Validation of a New Procedure for Determining Aromatics in Petroleum Distillates

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INITIAL VALIDATION OF A NEW PROCEDURE FOR DETERMINING AROMATICS IN PETROLEUM DISTILLATES

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ABSTRACT

The analytical data from an initial validation of a new method developed for determining aromatics in distillate fuels is reported. The method applies supercritical fluid chromatography (SFC) for the liquid chromatographic separation of total saturates and total aromatics, followed by flame ionization detection. A study was conducted to determine the validity of a SFC procedure after it was proposed to the Canadian national standard writing body for its adoption as a new standard method for determining aromatics. Inter-laboratory results suggest that SFC provides reproducible data among different laboratories and these SFC data correlate well with those obtained from other methods such as fluorescent indicator adsorption (FIA), nuclear magnetic resonance (NMR), and mass spectrometry (MS).

INTRODUCTION

In light of degrading feedstock qualities and increasing stringent environmental regulations, the oil industry faces greater challenges in combating long standing restraints of greater global energy demand and depleting conventional sources. The optimization of product quality and product performance become ever more critical to insure efficient and clean utilization of petroleum fuels. In Canada, where future fuel trend relies on increasing amount of domestic products derived from oil sands bitumens, heavy crudes and heavy oil deposits, product quality is being examined with caution. Compositional analysis of synthetic distillates shows considerably larger proportions of aromatics than normally present in conventional distillates (1) and the use of those products are of concern. The problems associated with combustion of highly aromatic fuels are widely documented and have prompted performance evaluations on various combustion equipment. Recently the Combustion and Carbonization Research Laboratory (CCRL) carried out a research program to study the influence of fuel quality on burner performance in residential heating appliances and to develop combustion technology for future Canadian fuels (2). During this study, it became apparent that a reliable analytical technique for determining fuel aromatics is critical for accurate interpretation of combustion performance data.

The method normally used for determining aromatics in oils is ASTM D1319, the fluorescent indicator adsorption (FIA) method (3), and it is well known for its simplicity and ease of operation. However, poor colour separation is usually observed for samples with final boiling points higher than 315°C and dark coloured samples, leading to less accurate results. Nuclear magnetic resonance (NMR) and mass spectroscopic (MS) techniques are powerful analytical tools which provide detailed structural information on fuel aromatics. They have not however received as wide an application as FIA by the oil industry due to their higher capital costs, long analysis times and requirement of specially trained operators. Several methods based on high performance liquid chromatography (HPLC) have been employed for saturates and aromatics determination (4,5). These methods are generally characterized by good separation, short analysis time, and adaptability to high boiling samples. Ultraviolet (UV) and refractive index (RI) detectors are commonly used for detection of the separated species, but extensive calibration of these detectors is required due to their specificity to compound types. Certain improvements have been made by using a dielectric constant (DC) detector which has a more uniform response (6). The flame ionization detector (FID) which is also a relatively uniform response detector over a wide range of hydrocarbon types, presents a problem when used with HPLC due to the interferences from commonly used solvents. The Evaporative Mass Detector is successfully used in the Fast Lube Separation (FLS) procedures but it is not amenable to lower boiling fractions including middle distillate fuels. There is a need to have a simple and reasonably fast method for aromatics determination in refinery applications. A general consensus from the oil industry indicates an increase in demand for hydrocarbon type analysis that can handle different refinery products and a requirement for analytical methods which are applicable to materials with wide boiling ranges (7). These requirements have led to the development of a new analytical technique utilizing supercritical fluid chromatography (SFC) by the author and coworkers (8). The method was developed by CCRL, of the Canadian Centre for Mineral and Energy Technology (CANMET), Energy, Mines, and Resources Canada through a private contractor. The application of SFC combined with FID for hydrocarbon type analyses was initially demonstrated by Norris and Rawdon (9) and Schwartz and Brownlee (10) for separation of saturates, olefins and aromatics in gasolines. The author's proposed method is applicable for determination of total aromatics in wide range of middle distillates including diesel fuels and heating fuels.

The method was originally proposed to the Canadian standards and specifications agency, the Canadian General Standards Board (CGSB) as a new standard for determining aromatics in petroleum middle distillates. CGSB then commissioned its Committee on Petroleum Test Methods to perform a preliminary round robin study on the proposed method and this paper describes the results from that study. Recently, the American Society for Testing and Materials (ASTM) incorporated the CANMET procedure as one of the SFC methods in the proposed ASTM designation for a standard method for determining aromatics in diesel fuels. The second level review is in progress at press time.

MATERIALS AND METHOD

Fuel Supply and Variety

Three Canadian oil companies contributed the fuels for this method validation study. The following samples were selected and designated as round robin (RB) for discussion purposes.

Participating Laboratories

One major Canadian oil company and two government research laboratories participated in the SFC analysis of 11 round robin samples. Confirmation analyses of the SFC data by FIA, NMR and MS were contributed by three other oil companies and two

TABLE 1. Middle distillate samples selected for method validation study

Sample	Sample type and crude source information
RB 1	Jet fuel type A1 processed from conventional Canadian and European pooled crudes
RB 2	Low pour diesel processed from Alberta interprovincial conventional sweet crude
RB 3	100% syncrude distillate processed from non-hydrotreated, conventional processing/fractionation products
RB 4	Jet fuel B containing over 90% of straight run products processed from Canadian conventional crude
RB 5	High density, high power diesel fuel from Western Canadian conventional crude
RB 6	Arctic diesel from a 25% cracked material, 75% straight run, 100% hydrodesulphurized, British Columbia light crude
RB 7	Distillate blend from synthetic and conventional crude
RB 8	Hydrotreated distillate from 100% synthetic crude
RB 9	Distillate containing cat-cracked components processed from conventional crude
RB 10	High boiling distillate containing cat-cracked components processed from conventional crude
RB 11	Low boiling commercial diesel fuel, source unknown

government research laboratories. Two of the laboratories performed repeatability tests of the SFC method using a number of quality control samples.

SFC Method and Instrumentation

All laboratories used SFC analytical procedures reported in reference (8) with minor modifications in operating conditions. As for the instrument, one laboratory utilized the SFC equipment fabricated in-house from existing laboratory equipment. It consisted of a Varian

Model 8500 Syringe pump to pressurize the carbon dioxide and a Shimazdu Model GC-8A gas chromatograph with flame ionization detector for chromatographic separation. The other two laboratories used commercial, Lee Scientific Model 600 SFC systems. Participants used the following instrumental conditions.

Standard conditions of the proposed method

CO_2 pressure:	3600 psi (245 atm)
Column temperature:	35°C
Detector temperature:	400°C
Column material:	silica, 5µm or 10µm
Column dimensions:	250 mm x 2.1 mm
Sample size:	0.2 µL
Sample injection:	1:10 (v/v) in carbon disulphide
Analysis time:	20 m

Minor modifications by Laboratories 1 and 4

CO_2 pressure:	3234 psi (220 atm) (Lab 4)
Column temperature:	40°C (Lab 4)
Column dimensions:	500 mm x 1.0 mm (Lab 1) 500 mm x 1.6 mm (Lab 4)
Sample size:	0.06 µL without dilution (Lab 4)
Analysis time:	40 m (Lab 4)

Other analytical methods

The round robin samples were also analyzed by fluorescent indicator adsorption (FIA) and proton nuclear magnetic resonance (1H NMR) techniques, which are commonly used by the industry for determining fuel aromatics. For FIA, the standard ASTM D1319 procedure was applied and the results were given in volumetric percentages (3). The aromatic weight per cent by NMR was calculated using hydrogen and carbon type distribution and formula-substructure relationships (11). One laboratory provided mass spectrometric data determined by a PONA method that provides concentrations of paraffins, olefins, naphthenes, and aromatics in the sample (12).

RESULTS AND DISCUSSIONS

SFC chromatograms and proton NMR spectra

The SFC chromatograms of three round robin samples are shown in Figures 1 to 3. Chromatograms of samples RB 1, RB 3, and RB 9 were selected and they were provided by Laboratory 1, Laboratory 2, and Laboratory 3 respectively. The first single peak in the chromatogram represents total saturates and it is followed by aromatic peaks. The notation "C" denotes the cut point between saturates and aromatics that was used to separate the peak areas. The first peak after the cut point represents monoaromatics. The second is for diaromatics and the following peaks represent various triaromatic components. Longer sample analysis time as indicated by 40 minutes retention time in the chromatograms of samples RB 1 was due to the longer chromatographic column used by Laboratory 1. The column was a 500 mm as compared to 250 mm that was used by the Laboratory 2. This longer time provided higher separation efficiency of hydrocarbons and as a result, individual peaks for mono-, di-, and triaromatics were obtained. If the total aromatics is of only interest, the analysis time can be reduced considerably by using a shorter column. The chromatogram of RB 9 was produced on a 500 mm column as well but took shorter analysis (20 minutes) due to a slightly higher column temperature. Concentrations of total aromatics

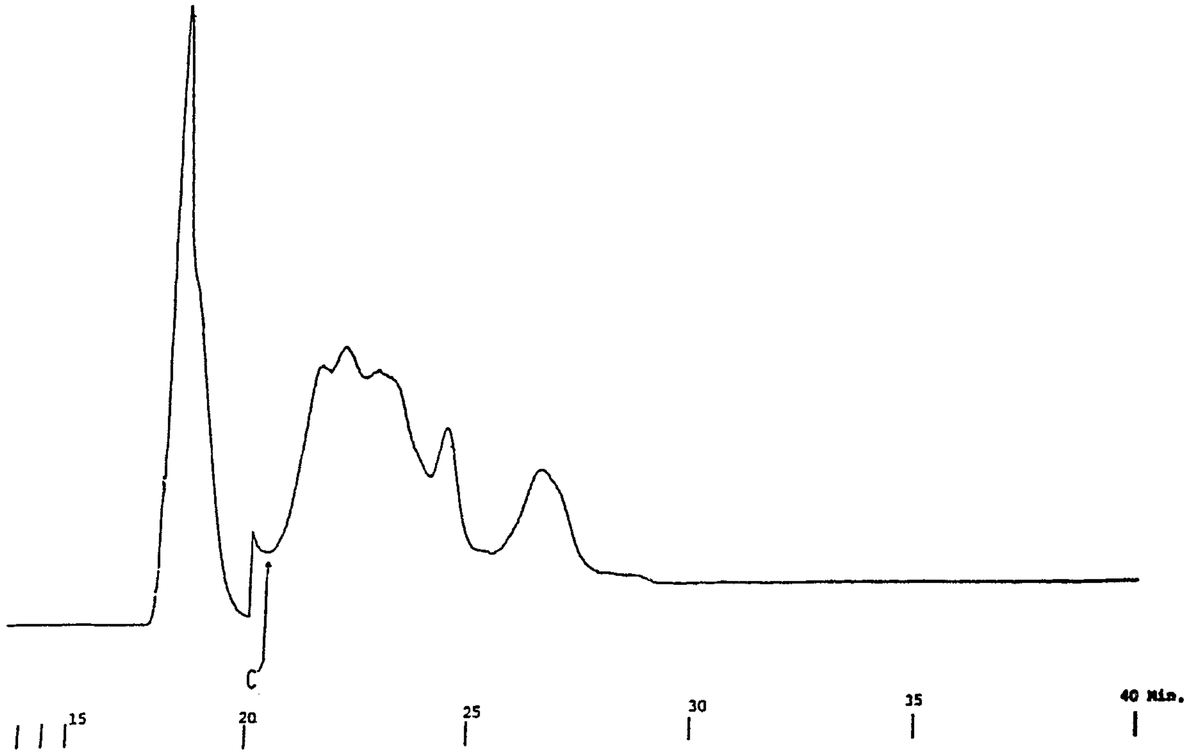

FIGURE 1. SFC CHROMATOGRAM OF SAMPLE RB 1 ON 500 MM COLUMN

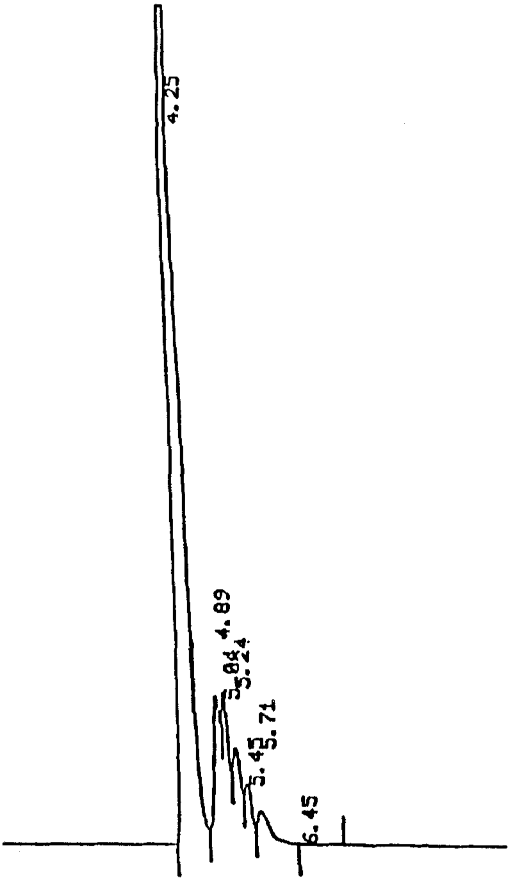

FIGURE 2. SFC CHROMATOGRAM OF SAMPLE RB 3 ON 250 MM COLUMN

in round robin samples were calculated from the NMR spectra similar to that of RB 2 shown in Figure 4.

Analytical Results

Aromatic contents of eleven round robin samples calculated from area percentages of the chromatograms are listed in Table 2. Each

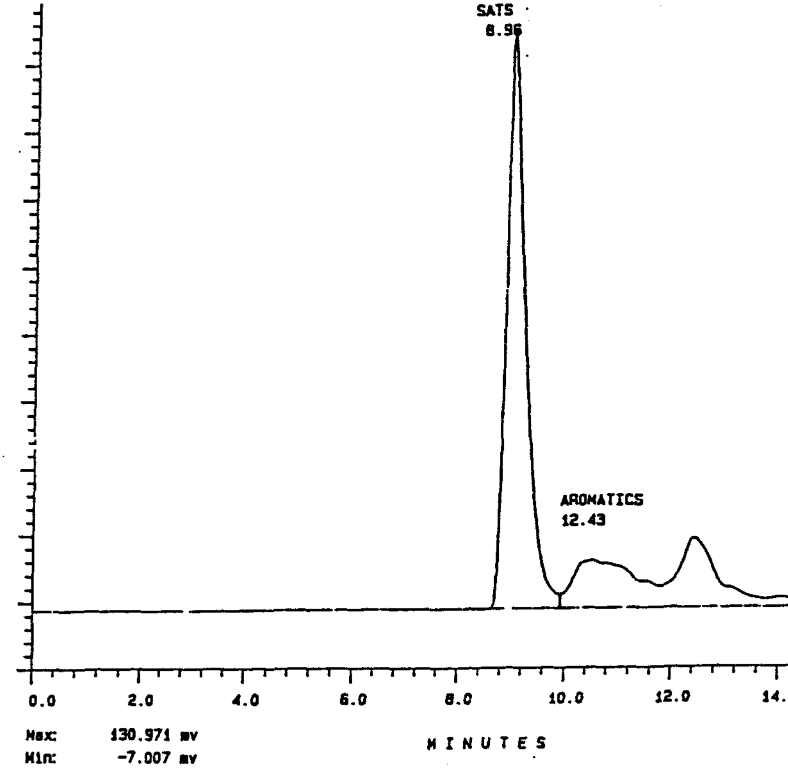

FIGURE 3. SFC CHROMATOGRAM OF SAMPLE RB 9 ON
INJECTED WITHOUT SAMPLE DILUTION

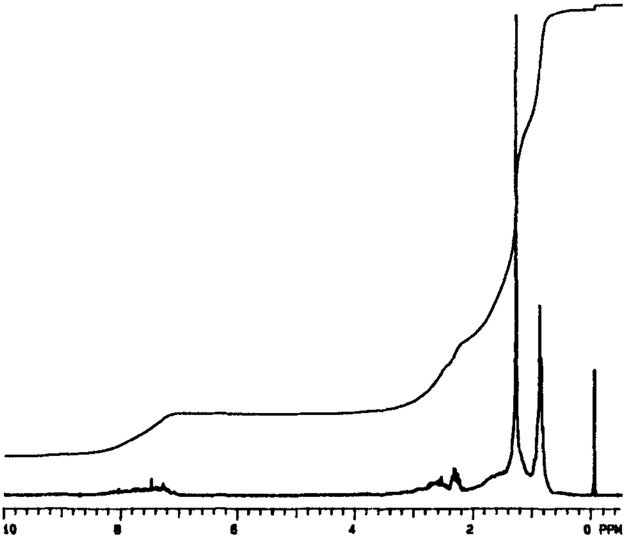

FIGURE 4. PROTON NMR SPECTRUM OF SAMPLE RB 2

TABLE 2. Total Aromatics of Round Robin Samples as Determined by Three Laboratories Using the SFC Method

Sample	Lab 1	Lab 1[a]	Lab 2	Lab 4	Lab 4[b]	Average[c]	RSD%
RB 1	20.5	19.1	22.8	20.5		21.3	6.2
RB 2	21.2	19.3	22.3	20.6		21.3	4.0
RB 3	42.4	39.8	46.2	40.0		42.9	7.3
RB 4	17.0	15.1	18.1	17.3		17.5	3.2
RB 5	36.1	33.1	38.2	34.2		36.2	5.5
RB 6	25.2	22.6	26.8	24.7		25.6	4.3
RB 7	38.3		40.3	40.9	36.6	39.2	5.0
RB 8	15.8		14.2	18.8	13.1	15.5	16
RB 9	41.3		40.2	39.4	38.0	39.7	3.5
RB 10	33.9		31.6	34.1	30.6	32.6	5.3
RB 11	28.1		27.3	28.9	26.2	27.6	4.2

a at column temperature 30°C and CO_2 pressure 1690 psi
b sample injected without dilution with CS_2
c averaging did not include results from Lab 1[a]

result represents the average value of a minimum of two SFC runs. The three data sets showed good agreement with an average relative standard deviation of 5.2, although there were slight differences in experimental conditions. Laboratory 1 also analyzed six selected samples (RB 1-6) using slightly different column temperature and CO_2 pressure as outlined in one of the methods under ASTM's review. These results (column Lab 1^a) are slightly lower than those obtained using the procedure in the proposed method. Similarly, slightly lower results (column Lab 4^b) are observed by Laboratory 4 on other samples (RB 7-11), when sample were injected directly without ten fold dilution with CS2, as required by the proposed method. Laboratory 1 feels that the use of a longer column provides better information on aromatic types and the extra analysis time is worth investing. At the same time, Laboratory 2 followed strict conditions outlined in the proposed method and proved that the speed of the analysis (lower operation cost) and applicability of the method to any fabricated SFC unit (lower capital cost) are two attractive features that outweigh other techniques. Laboratory 3, however, has reservations about dilution of samples with CS_2, before injection. A slight signal contribution in the chromtographic region from a pure CS_2 injection was observed by the laboratory and it suggested that this disturbance might have been responsible for 1 to 2% increase in aromatics results. Despite this observation, results from all three laboratories are generally comparable and appear to be within the experimental error of the method.

Table 3 reports the FIA results of round robin samples as determined by four laboratories. Samples RB 1-6 were analyzed by only one laboratory. The overall relative standard deviation of FIA

TABLE 3. Total Aromatics of Round Robin Samples as Determined by Four Laboratories Using the FIA Method

Sample	Lab 3	Lab 5	Lab 6	Lab 7	Average	RSD%
RB 1	18.9				18.9	
RB 2	19.7				19.7	
RB 3	41.6				41.6	
RB 4	13.5				13.5	
RB 5	32.1				32.1	
RB 6	22.8				22.8	
RB 7	38.2	36.7	38.2	33.1	36.6	6.5
RB 8	16.5	18.8	17.5	14.2	16.8	12
RB 9	38.2	32.0	41.0	40.4	37.9	11
RB 10	29.6	37.0	34.0	26.0	31.7	15
RB 11	26.1	25.4	26.0	24.4	25.5	3.1

results are larger than those provided by SFC method. This indicates the higher degree of reliability of SFC method over the FIA method.

In Table 4, data from four different analytical techniques are reported. While absolute comparison of results are not appropriate due to differences in intrinsic nature of individual technique, some observations may be made. Data show good correlations between SFC, FIA and NMR results with the exception of an outlier (RB 9) in NMR data. MS data provided by one particular PONA method appears the least comparable with SFC as well as the other two methods. It should be noted that MS results cannot be considered as actual weight per cent since data are derived from the number of ion counts of various hydrocarbons. It appears from the lack of a definite trend in deviation of MS data from the rest that the discrepancy could be more laboratory or method dependent rather than the MS technique

TABLE 4. Comparison of SFC, FIA, NMR and MS data

Sample	SFC, wt% (average)	NMR, wt% (Lab 3)	MS, % (Lab 1)	FIA, vol% (average)
RB 1	21.3	19.4	17.3	18.9
RB 2	21.3	20.9	17.6	19.7
RB 3	42.9	35.0	32.3	41.6
RB 4	17.5	18.9	30.2	13.5
RB 5	36.2	32.9	28.2	32.1
RB 6	25.6	24.0	40.5	22.8
RB 7	39.2	38.6	43.4	36.6
RB 8	15.5	20.2	26.3	16.8
RB 9	39.7	22.6*	40.7	37.9
RB 10	32.6	33.3	29.3	31.7
RB 11	27.6	29.5	25.2	25.5

* apparent outlier and was not included in linear correlation

itself. The analytical results in Table 4 gave the following statistical values.

Methods	Linear correlation coefficient	slope of the regression line
SFC (wt %) vs NMR (wt %)	0.947	0.75
SFC (wt %) vs MS (%)	0.571	0.52
SFC (wt %) vs FIA (vol %)	0.988	0.97

A good correlation between SFC and FIA perhaps will convince the oil industry to easily accept the SFC method as a new standard method for determining total aromatics in petroleum distillates. The data also provide an important conclusion, i.e., validity of SFC results is confirmed by the conventional FIA method as well as by the

TABLE 5. Repeatability of SFC method

Sample	Wt% aromatics from multiple analyses	RSD%
RP 1	77.8 77.6 77.7 77.7	0.1
RP 2	52.8 52.9 52.5	0.4
RP 3	22.2 21.5 21.5 22.6 22.7 23.5 21.1	4.4
RP 4	36.2 38.3 39.0 38.7 39.2	3.3
RP 5	27.5 30.2 32.4 29.0 27.4 28.9 30.0 30.1 29.1	5.1
RP 6	32.7 31.9 32.7 32.8	1.2
RP 7	42.7 42.7 42.3 42.5	0.5
RP 8	22.3 22.3 22.8 22.7 21.8	1.8
RP 9	22.1 21.8 21.4	1.8

instrumental NMR method. A detailed investigative report on correlations among SFC, NMR, FIA and MS, using larger number of test samples has been published by the author recently (13). In that study, SFC data correlates best with NMR data followed by FIA data.

The repeatability of the proposed SFC method was also examined. Two laboratories performed multiple analyses of eight selected samples and results as shown in Table 5. Coefficient of variation or relative standard deviation (RSD) of results vary from 0.1% to 5.1%, with half of the data having less than 2%.

CONCLUSIONS

Independent SFC analyses of eleven fuels by three participating laboratories showed very good agreement. The SFC aromatics weight per cent data agree well with those determined using the NMR method. A good correlation between SFC weight per cent and FIA volume per cent results is also observed. The repeatability of the SFC method is good as evidenced by excellent (0.1-5%) relative standard deviation of analytical results. The success of this procedure is mainly contributed by the uniform response of the flame ionization detector and by the excellent liquid chromatographic separation of SFC. The proposed SFC method can be used on all types of SFC equipment, commercial or modified laboratory equipment.

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