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Canadian General Standards Board | Office des normes générales du Canada

CAN/CGSB-3.0
No./Nº 15.0-2002

ICS 75.040.50

WITHDRAWAL

December 2016

Methods of testing petroleum and associated products
Standard test method for the determination of aromatic hydrocarbons by their ring number in petroleum middle distillates by supercritical fluid chromatography

This National Standard of Canada is hereby withdrawn due to limited use and support for its revision.

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RETRAIT

Décembre 2016

Méthodes d'essai des produits pétroliers et produits connexes
Méthode normalisée de dosage des hydrocarbures aromatiques, en fonction du nombre de cycles, dans les distillats moyens de pétrole, par chromatographie en fluide supercritique

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No./N° 15.0-2002
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February/Février 2004

ICS 71.040.50

CANADIAN GENERAL STANDARDS BOARD

METHODS OF TESTING PETROLEUM AND ASSOCIATED PRODUCTS

STANDARD TEST METHOD FOR THE DETERMINATION OF AROMATIC HYDROCARBONS BY THEIR RING NUMBER IN PETROLEUM MIDDLE DISTILLATES BY SUPERCRITICAL FLUID CHROMATOGRAPHY

Title

Change the title of this test method to read:

Standard Test Method for the Determination of Aromatic Hydrocarbons by Their Ring Number in Petroleum Naphthas and Middle Distillates by Supercritical Fluid Chromatography

1. SCOPE

1.3 Change this paragraph to read:

This test method is applicable to petroleum fractions in the boiling range of 25 to 385°C, including those with dark coloration. However, precision has only been determined for middle distillate fuels, not for naphthas or other hydrocarbon streams outside the normal distillation range of middle distillates.

1.4 This change applies to French only.

OFFICE DES NORMES GÉNÉRALES DU CANADA

MÉTHODES D'ESSAI DES PRODUITS PÉTROLIERS ET PRODUITS CONNEXES

MÉTHODE NORMALISÉE DE DOSAGE DES HYDROCARBURES AROMATIQUES, EN FONCTION DU NOMBRE DE CYCLES, DANS LES DISTILLATS MOYENS DE PÉTROLE, PAR CHROMATOGRAPHIE EN FLUIDE SUPERCRITIQUE

Titre

Modifier le titre de cette méthode d'essai comme suit:

Méthode normalisée de dosage des hydrocarbures aromatiques, en fonction du nombre de cycles, dans les naphthas et les distillats moyens de pétrole, par chromatographie en fluide supercritique

OBJET

Modifier ce paragraphe comme suit:

La présente méthode d'essai s'applique aux fractions de pétrole dont le point d'ébullition se situe entre 25 et 385°C, y compris les fractions foncées. Cependant, la justesse n'a été déterminée que pour les combustibles de distillat moyen, et non pour les naphthas ou autres hydrocarbures à l'extérieur de l'intervalle normal de distillation des distillats moyens.

Modifier ce paragraphe comme suit:

Les hydrocarbures saturés sont d'abord séparés des hydrocarbures aromatiques, puis les hydrocarbures aromatiques sont fractionnés sur une colonne capillaire remplie de silice, selon le nombre de cycles benzéniques qu'ils contiennent.

Withdrawn/Retired

2. REFERENCED PUBLICATION

2.2 Change this paragraph to read:

A dated reference in this method is to the issue specified. An undated reference in this method is to the latest issue, unless otherwise specified by the authority applying this method. The sources are given in the Notes section.

3. SUMMARY OF TEST METHOD

3.1 Change the first sentence of this paragraph to read:

A hydrocarbon sample is injected onto the silica chromatographic column and eluted using supercritical fluid carbon dioxide mobile phase.

4. SIGNIFICANCE AND USE

4.1 Change the second sentence of this paragraph to read:

Total aromatic hydrocarbon content and monoaromatic,[1] diaromatic[2] and polyaromatic[3] hydrocarbon components of naphthas and middle distillate fuels (jet, diesel) can be determined more rapidly and at lower cost than Mass Spectroscopic techniques.

5. APPARATUS

5.1.1 ***Chromatographic columns***

Change the first sentence of this paragraph to read:

Chromatographic columns: a 4.6 × 250 mm column packed with silica (5 µm diameter) is used.

9. PRECISION[5] AND BIAS

Add the following new par. 9.1.3:

9.1.3 The precision of this test method for naphthas and hydrocarbon streams outside the normal range of middle distillates has not been determined.

PUBLICATION DE RÉFÉRENCE

Modifier ce paragraphe comme suit:

Toute référence datée dans la présente méthode renvoie à l'édition mentionnée. Sauf indication contraire de l'autorité appliquant la présente méthode, toute référence non datée dans cette dernière renvoie à l'édition la plus récente. Les sources de diffusion sont indiquées dans la section intitulée Remarques.

RÉSUMÉ DE LA MÉTHODE D'ESSAI

Modifier la première phrase de ce paragraphe comme suit:

On injecte un échantillon d'hydrocarbure dans la colonne chromatographique remplie de silice, puis on l'élue au moyen du dioxyde de carbone supercritique comme phase mobile.

PORTÉE ET UTILISATION

Modifier la deuxième phrase de ce paragraphe comme suit:

Elle permet de doser les hydrocarbures aromatiques totaux et les hydrocarbures aromatiques monocycliques,[1] dicycliques[2] et polycycliques[3] dans les naphthas et les combustibles de distillats moyens (carburéacteur, carburant diesel) plus rapidement et à un coût moindre que les techniques de spectroscopie de masse.

APPAREILLAGE

Colonnes chromatographiques

Modifier la première phrase de cet alinéa comme suit:

Colonnes chromatographiques: on utilise une colonne de 4.6 × 250 mm remplie de silice (5 µm de diamètre).

JUSTESSE[5] ET ERREUR SYSTÉMATIQUE

Ajouter le nouvel al. 9.1.3 suivant:

La justesse de cette méthode d'essai pour les naphthas et les hydrocarbures à l'extérieur de l'intervalle normal de distillation des distillats moyens n'a pas été déterminée.

Withdrawn/Retirée

10. NOTES

10.2 Source of Referenced Publications

Change this paragraph to read:

Source of Referenced Publications — The publications referred to in par. 2.1.1 and 10.1 may be obtained from ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, U.S.A., telephone (610) 832-9585, fax (610) 832-9555, Web site www.astm.org, or from IHS Canada, 1 Antares Drive, Suite 200, Ottawa, Ontario K2E 8C4, telephone (613) 237-4250 or 1-800-267-8220, fax (613) 237-4251, e-mail gic@ihscanada.ca.

REMARQUES

Source de diffusion des publications de référence

Modifier ce paragraphe comme suit:

Source de diffusion des publications de référence — Les publications mentionnées à l'al. 2.1.1 et au par. 10.1 sont diffusées par ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, U.S.A., téléphone (610) 832-9585, télécopieur (610) 832-9555, site Web www.astm.org, ou par IHS Canada, 1, promenade Antares, pièce 200, Ottawa (Ontario) K2E 8C4, téléphone (613) 237-4250 ou 1-800-267-8220, télécopieur (613) 237-4251, courriel gic@ihscanada.ca.

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Canadian General Standards Board
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No. 15.0-94

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Methods of Testing Petroleum and Associated Products

Standard Test Method for the Determination of Aromatic Hydrocarbons by Their Ring Number in Petroleum Middle Distillates by Supercritical Fluid Chromatography

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NATIONAL STANDARD OF CANADA

CAN/CGSB-3.0
No. 15.0-2002

Supersedes CAN/CGSB-3.0
No. 15.0-94

METHODS OF TESTING PETROLEUM AND ASSOCIATED PRODUCTS

STANDARD TEST METHOD FOR THE DETERMINATION OF AROMATIC HYDROCARBONS BY THEIR RING NUMBER IN PETROLEUM MIDDLE DISTILLATES BY SUPERCRITICAL FLUID CHROMATOGRAPHY

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Canadian General Standards Board

Approved by the
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Acknowledgment is made for the translation of this National Standard of Canada by the Translation Bureau of Public Works and Government Services Canada.

National Standard of Canada

CGSB Ottawa Canada K1A 1G6	**METHODS OF TESTING PETROLEUM AND ASSOCIATED PRODUCTS**	**CAN/CGSB-3.0**
	Standard Test Method for the Determination of Aromatic Hydrocarbons by Their Ring Number in Petroleum Middle Distillates by Supercritical Fluid Chromatography	**No. 15.0-2002**

Supersedes CAN/CGSB-3.0
No. 15.0-94

Withdrawn/Retiree

1. SCOPE

1.1 This method provides for the determination of the mass percentage of saturates, monoaromatics, diaromatics and polyaromatics in petroleum fractions that distil below 385°C. The distillates should consist primarily of hydrocarbons and should not contain significant amounts of heteroatoms such as nitrogen, sulphur and oxygen. This method does not apply to samples that contain olefins. Olefins elute primarily in the saturate region but not exclusively, therefore any olefins in the samples will introduce a bias.

1.2 This test method utilizes supercritical fluid chromatography (SFC) for the separation of hydrocarbons and flame ionization detection (FID) for quantitative analysis.

1.3 This test method is applicable to petroleum fractions in the boiling range of 25 to 385°C, including those with dark coloration.

1.4 Saturates are initially separated from the aromatics and the aromatics are then further fractionated, according to number of aromatic rings, on a packed silica column.

1.5 The testing and evaluation of a product against this method may require the use of materials and/or equipment that could be hazardous. This document does not purport to address all the safety aspects associated with its use. Anyone using this method has the responsibility to consult the appropriate authorities and to establish appropriate health and safety practices in conjunction with any applicable regulatory requirements prior to its use.

2. REFERENCED PUBLICATION

2.1 The following publication is referenced in this method:

2.1.1 ASTM International

E 691 — Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method.

2.2 A reference to a regulation is always to the latest issue. A dated reference is to the issue specified. An undated reference is to the latest issue, unless otherwise specified by the authority applying this method. The sources are given in the Notes section.

3. SUMMARY OF TEST METHOD

3.1 A middle distillate sample is injected onto the silica chromatographic column and eluted using supercritical fluid carbon dioxide mobile phase. Mass percentages of total saturates, monoaromatics, diaromatics and polyaromatics are calculated from their corresponding peak areas on the chromatogram. The cut points between each component type are defined by using the retention times of components in a reference mixture of model compounds (par. 6.3).

4. SIGNIFICANCE AND USE

4.1 This method is intended for use in petroleum testing analytical laboratories. Total aromatic hydrocarbon content and monoaromatic,[1] diaromatic[2] and polyaromatic[3] hydrocarbon components of middle distillate fuels (jet, diesel) can be determined more rapidly and at lower cost than Mass Spectroscopic techniques. The current standard for fuel aromatics, Fluorescent Indicator Adsorption method, ASTM D 1319, is incapable of quantitating the aromatics by ring number.

5. APPARATUS

5.1 **Supercritical fluid chromatography instrument (SFC):** a commercial SFC instrument equipped with a flame ionization detector that meets the performance requirements of section 7. The system may be equipped with either manual injection or with an autosampler.

5.1.1 ***Chromatographic columns:*** a 4.6 × 250 mm packed silica column (5 µm) is used. The column should provide a resolution of 10 in the separation of saturates and monoaromatic hydrocarbons. Other suitable liquid or supercritical fluid chromatographic columns that provide separation of saturates and mono-, di- and polyaromatic hydrocarbons, and meet the performance requirements of section 7 may be used.

5.1.2 ***Restrictor:*** check the height of the restrictor in order to obtain a relative carbon response of one plus or minus two percent of the reference mixture.

6. MATERIALS

6.1 **Supercritical carbon dioxide:** pressurized commercial cylinders of supercritical fluid chromatographic grade, 99.99% purity carbon dioxide liquid.

6.2 **Carbon disulphide:** ACS grade carbon disulphide of 99% purity is used for the preparation of reference mixtures. Caution is required in handling this reagent since it is extremely flammable and toxic (please review material safety data sheet prior to use).

6.3 **Reference mixture:** a mixture of model compounds, containing 15 mass percent each, with the exception of docosane at 10 mass percent, is used to determine retention times of typical hydrocarbon types. The described amounts of docosane (n-C_{22}), 2-ethyl toluene, tetralin, naphthalene, dibenzothiophene, anthracene and pyrene are prepared in a known amount of carbon disulphide. The concentration level should be 0.01 g of component per millilitre of carbon disulphide as a suitable dilution ratio.

6.4 **Quality control sample:** a mixture containing known hydrocarbon compounds or a real petroleum distillate sample that can be used to evaluate instrument performance.

6.5 **Air:** hydrocarbon-free compressed air is used for the FID.

6.6 **Hydrogen:** hydrocarbon-free hydrogen gas is used as the fuel for the FID.

7. PROCEDURE

7.1 **Preparation of Apparatus** — Install the SFC equipment according to the manufacturer's instructions. Typical system operating conditions are described in Table 1. Optimum conditions will depend upon the column used, operating conditions and the system performance assessment.

7.2 **System Performance** — Prior to sample analysis, the SFC instrument performance must be assessed using the reference mixtures described in par. 6.3. Necessary corrections and adjustments to the temperature, pressure and flow rates or column should be made if the performance criteria for retention time and resolution are not within the limits.

---

[1] *Hydrocarbons containing one aromatic ring structure such as alkyl benzenes.*

[2] *Hydrocarbons containing two aromatic ring structures such as alkyl naphthalenes.*

[3] *Hydrocarbons containing three or more aromatic ring structures such as alkyl anthracenes.*

Withdrawn/Retirée

7.2.1 ***Repeatability of Retention Times***[4] — Analyze the reference mixture to determine the retention times of hydrocarbon compounds. Repeat injections should have a retention time repeatability of 0.5% or less for the n-C_{22} and 2-ethyl toluene peak times.

Typical retention times of some model compounds are reported in Table 2, the corresponding chromatogram is shown in Figure 1.

7.2.2 ***Resolution*** — Chromatographic resolution of any peak pairs can be calculated from the analysis of the reference mixture using the following formula:

$$R = \frac{1.18\ dT}{(W_1 + W_2)}$$

where:

R = peak resolution
dT = retention time in minutes of $peak_2$ minus retention time in minutes of $peak_1$
W_1 = peak width at half height in minutes for $peak_1$
W_2 = peak width at half height in minutes for $peak_2$

The resolution between the saturates and monoaromatics should be at least ten, and between the monoaromatics and polyaromatics at least eight.

7.3 **Detector Accuracy Check** — The carbon response of the FID detector is determined from the analysis of the reference mixture. Calculate the response factor, relative to docosane for each of the components using the following formula:

$$RCR_i = \frac{\left(\frac{M_{C22}}{M_i}\right) \times \left(\frac{A_i}{A_{C22}}\right)}{\left(\frac{12.01 \times n_i}{MM_i}\right) \times \left(\frac{310.61}{12.01 \times 22}\right)}$$

where:

RCR_i = relative carbon response for component i
M_{C22} = mass in grams of docosane
M_i = mass in grams of component i
A_i = area of component i in the reference mixture
A_{C22} = area of docosane in the reference mixture
12.01 = atomic mass of carbon
n_i = number of carbon atoms in the component i molecule
MM_i = molecular mass of the component i
310.61 = molecular mass of docosane
22 = number of carbon atoms in the docosane molecule

The relative response factors for the components should be within 2%, with the exception of dibenzothiophene, which is lower due to the sulphur. Adjust the restrictor position in the FID until these values are met.

7.4 **Analysis Procedure**

7.4.1 Maintaining the optimal operating conditions determined above, analyze the reference mixture, the quality control sample and the samples. Insert a reference mixture and a quality control or previously analyzed sample at the beginning, middle and at the end of a series of samples. The results for the reference mixture shall meet the requirements of par. 7.3 and the quality control shall meet the repeatability requirements listed in section 9.

7.4.2 Record the chromatogram until the sample has completely eluted from the column. The endpoint is defined by the detector signal returning to baseline and remaining there, after the elution of the polyaromatics. Due to the low concentration of polyaromatics in some samples, the chromatogram should be checked to verify that the integrated areas in this region are valid, and not due to signal noise or carry-over from the previous sample. A diode array

[4] *The retention times may vary from the values of Table 2, if different instrument operating conditions are used.*

Withdrawn/Retiree

detector is useful in confirming the presence of small quantities of polyaromatics. Figure 2 is a typical chromatogram of a diesel fuel. The chromatogram generally consists of a relatively sharp peak for the saturates and one or more broad peaks for the aromatics.

7.4.3 From the chromatogram of the reference mixture, note the retention times of the hydrocarbons, typical retention times for these compounds are reported in Table 2, and determine the cut-points between the monoaromatics and diaromatics and between the diaromatics and polyaromatics. The monoaromatic/diaromatic cutpoint is at the midpoint between the tetralin and the naphthalene peaks, calculated by adding the retention times of the two peaks and dividing by 2. The diaromatic/polyaromatic cutpoint is at the midpoint between the dibenzothiophene and the anthracene peaks.

7.4.4 Integrate the total area of the sample chromatogram from the beginning of the first peak to the return to baseline at the end. The lowest part of the valley between the saturates and aromatic peaks (between the retention times of docosane and 2-ethyl toluene) is defined as the saturates/monoaromatics cutpoint.

7.4.5 The integrated area from the beginning of the first peak to the saturate/monoaromatic cutpoint is assigned to the saturates; the integrated area between the saturate/monoaromatic and monoaromatic/diaromatic cutpoints to the monoaromatics; the integrated area between the monoaromatic/diaromatic and the diaromatic/polyaromatic cutpoints to the diaromatics; and the integrated area from the diaromatic/polyaromatic cutpoint to the endpoint to the polyaromatics.

8. CALCULATION OF RESULTS

8.1 The mass percentage for saturates is calculated as the saturate area divided by the total area times 100. The mass percentage for the aromatic hydrocarbon groups is calculated in a similar fashion.

8.2 **Reporting** — Report the mass percentage concentrations of the hydrocarbon groups to the nearest one tenth of a percent (0.1%).

9. PRECISION[5] AND BIAS

9.1 The precision of the procedure in this test method for determining the aromatic hydrocarbons by their ring number in middle distillates by supercritical fluid chromatography as determined by the statistical examination of interlaboratory test results is as follows:

9.1.1 ***Repeatability*** — The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method exceed the following values only in one case in twenty:

Repeatability:

For monoaromatics: $r = 0.032 \times \text{mass \%}$
For diaromatics: $r = [0.038 \times \text{mass \%}] + 0.431$
For polyaromatics: $r = [0.772 \times \text{mass \%}] + 0.5$

9.1.2 ***Reproducibility*** — The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following values only in one case in twenty:

Reproducibility:

For monoaromatics: $R = 0.270 \times \text{mass \%}$
For diaromatics: $R = [0.224 \times \text{mass \%}] + 5.42$
For polyaromatics: $R = [1.70 \times \text{mass \%}] + 0.67$

[5] *Repeatability and reproducibility were calculated by the statistical examination of interlaboratoy test results according to the procedures described in ASTM E 691. A technical report on this interlaboratory study would be made available through the Business Office of the CANMET Energy Technology Centre – Ottawa, Natural Resources Canada. The equations for r and R for all aromatic types were derived by modelling of test results representing samples having 8 to 44% total aromatics by mass.*

Withdrawn/Retirée

9.2 **Bias** — Since there is no accepted reference material suitable for determining bias for the procedure in this test method, bias cannot be determined.

10. NOTES

10.1 **Related Publications**

D 1319 — Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption

D 4057 — Standard Practice for Manual Sampling of Petroleum and Petroleum Products

D 4307 — Standard Practice for Preparation of Liquid Blends for Use as Analytical Standards

D 5186 — Standard Test Method for Determination of the Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels and Aviation Turbine Fuels by Supercritical Fluid Chromatography

D 6299 — Standard Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance

E 355 — Standard Practice for Gas Chromatography Terms and Relationships.

10.2 **Source of Referenced Publications** — The publications referred to in par. 2.1.1 and 10.1 may be obtained from the ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, U.S.A., or from IHS Canada, 240 Catherine Street, Suite 305, Ottawa, Ontario K2P 2G8, telephone (613) 237-4250 or 1-800-854-7179, fax (613) 237-4251.

TABLE 1

Supercritical Fluid Chromatography Operational Conditions

Column	Silica
Length, mm	250
Inside diameter, mm	4.6
Particle size, µm	5
Temperature, °C	35
CO_2 pressure, Mpa	15.0
Injector temperature, °C	25
FID temperature, °C	250
Airflow rate, mL/min	350
H_2, mL/min	40
N_2, mL/min	27
CO_2 flowrate, mL/min	2

Withdrawn/Retirée

TABLE 2

Retention Times of Model Compounds
Established Under Instrumental Conditions Reported in Table 1

Compound	Hydrocarbon Type	Retention Time, min
Docosane	n-Alkane	1.45
2-Ethyl toluene	Monoaromatic	2.19
Tetralin*	Monoaromatic	2.60
Naphthalene	Diaromatic	3.10
Dibenzothiophene	Diaromatic	5.13
Anthracene	Polyaromatic	5.42
Pyrene	Polyaromatic	7.94

*(1,2,3,4-Tetrahydronaphthalene)

Withdrawn/Retirée

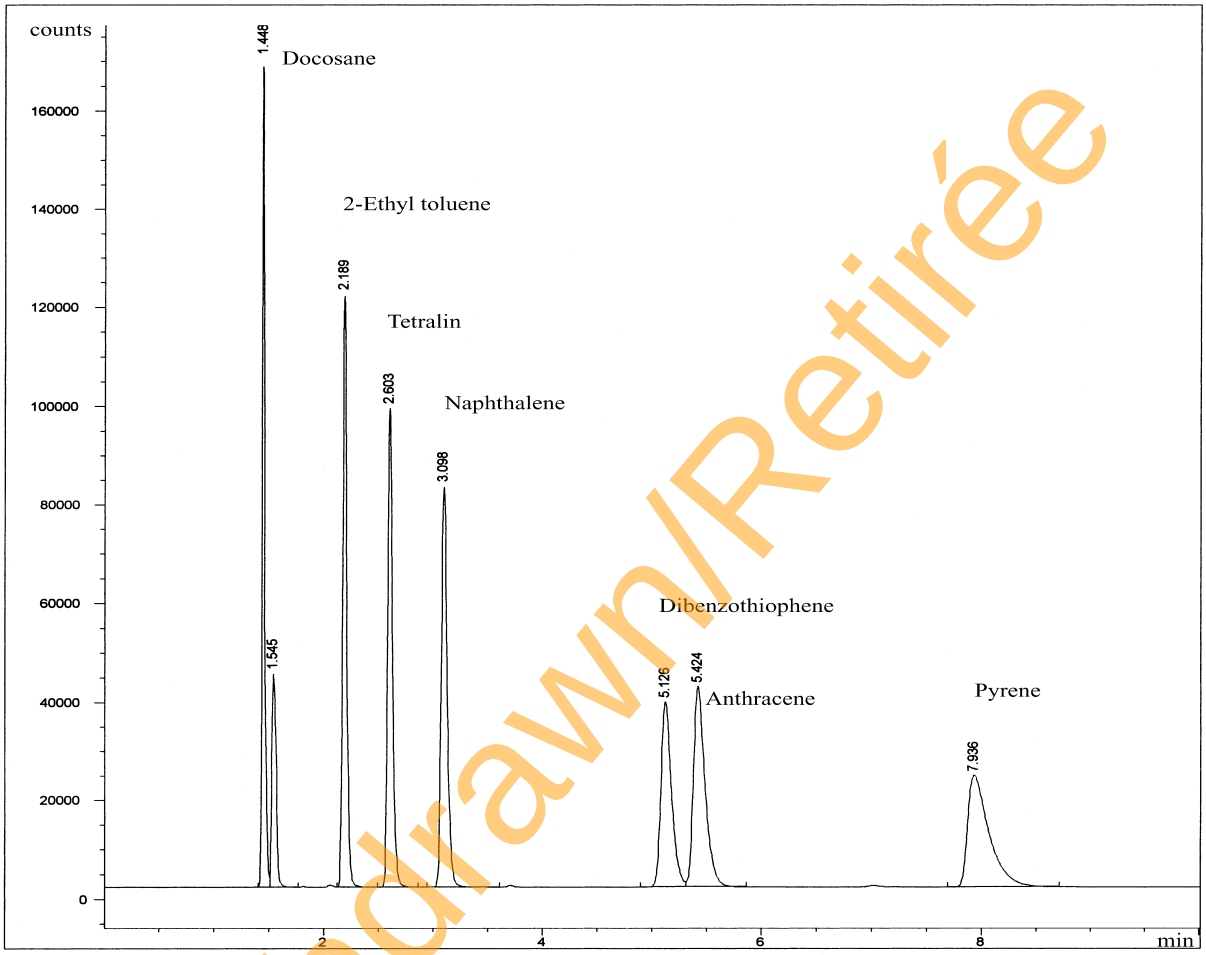


FIGURE 1

Supercritical Fluid Chromatogram of the Reference Mixture for Determination of Retention Times and Cut-points

Withdrawn/Retirée

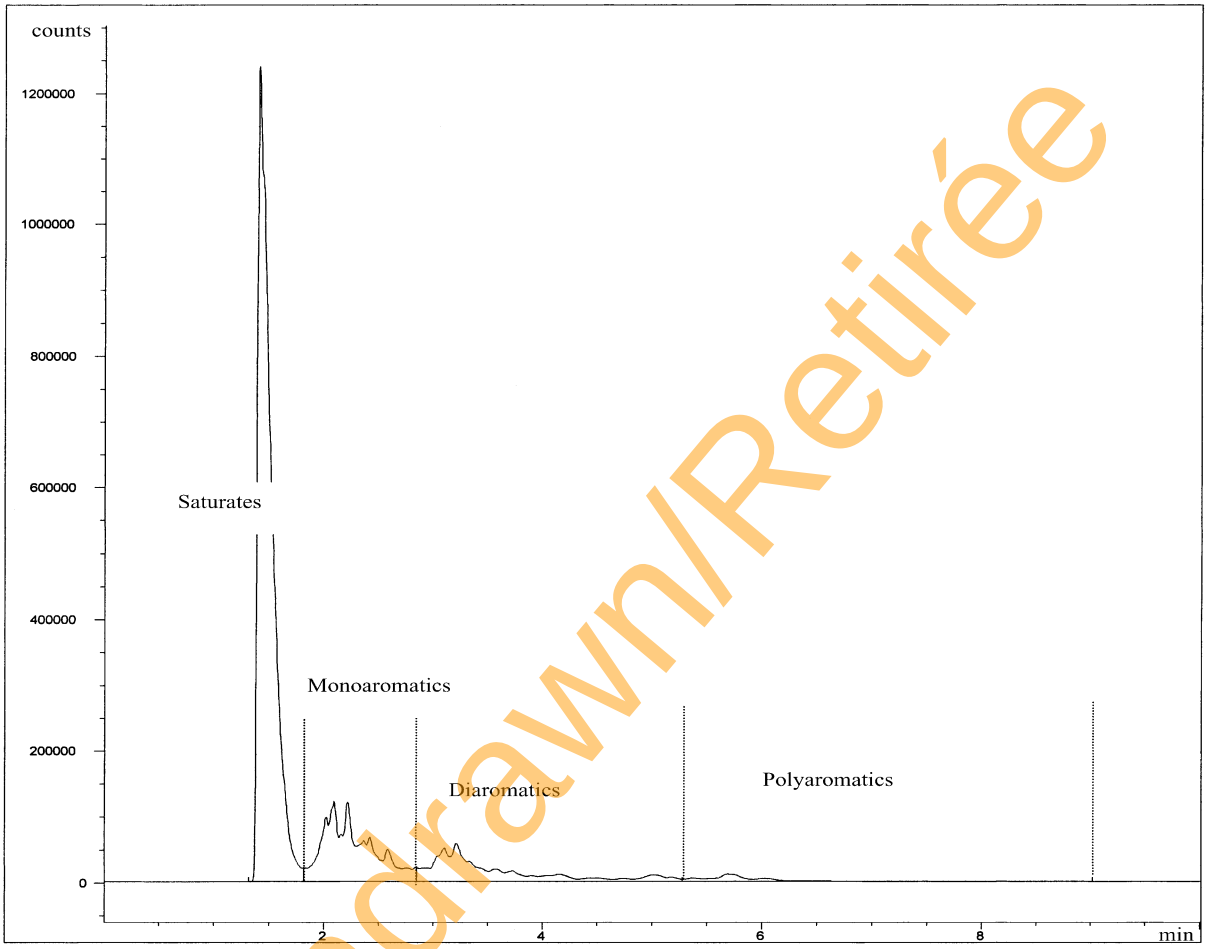


FIGURE 2

Typical Supercritical Fluid Chromatogram of a Diesel Fuel

Withdrawn/Retirée