a review of analytical methods for the quantification of aromatics in diesel fuels

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P. Heinze (Chairman)

W. E. Betts
M. Booth
P. Gadd
F. Giavazzi
H. Guttman
D. E. Hall
R. F. Mayers
R. Mercogliano

R. C. Hutcheson (Technical Coordinator)

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ABSTRACT

The definition of "aromatics" in diesel fuel has caused difficulties, both within the oil industry and amongst other interested parties. By virtue of the boiling range of the fuel, the majority of its hydrocarbons will have between ten and twenty carbon atoms. This means that any molecule considered aromatic may also have a "non-aromatic" component that is greater than the aromatic portion. The level of aromatics that is measured is therefore dependent on the technique used. This report summarizes the various analytical procedures currently available for the determination of diesel fuel "aromaticity".

KEYWORDS

Diesel fuel, aromatics, aromaticity, analytical methods, chromatography, mass spectrometry, spectroscopy

NOTE

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SUMMARY

The definition of "aromatics" in diesel fuel has caused difficulties, both within the oil industry and amongst other interested parties. By virtue of the boiling range of the fuel, the majority of its hydrocarbons will have between ten and twenty carbon atoms. This means that any molecule considered aromatic may also have a "non-aromatic" component that is greater than the aromatic portion. The level of aromatics that is measured is therefore dependent on the technique used.

A large number of methods are available for the determination of aromatics in petroleum distillates. Many of the methods have been formalized as IP and/or ASTM standards. The complexity of both the methods and instrumentation vary considerably, as do the precision and cost of analysis.

This report summarizes the various analytical procedures currently available for the determination of diesel fuel "aromaticity". It concludes that supercritical fluid chromatography (SFC) and high performance liquid chromatography (HPLC) are the most attractive current options. HPLC is a more established technique and also offers both total and aromatic-type compositional data

1. INTRODUCTION

The definition of 'aromatics' within the context of diesel fuel has caused problems, both within the oil industry, for the analysts who test and quantify them, and outside the industry, for those who need to interpret the data.

Aromatics are chemically defined as the class of compounds derived from benzene (C_6H_6) which contain a closed ring of six carbon atoms. The term 'aromatic' also applies to other ring compounds, often containing heteroatoms, which have a fully-conjugated double bond system. Aromatic compounds may also have more than one ring in their structure and may have aliphatic chains or rings attached to one or more of the basic rings.

The latter category is of great importance when the aromatic content of diesel is considered. By virtue of the boiling range of the fuel, the majority of the hydrocarbons will have between ten and twenty carbon atoms. If the single ring aromatic compounds are considered, it can be seen that the aliphatic chain could be from four to fourteen carbon atoms in length. This means that any molecule considered aromatic may also have a 'non-aromatic' component either equal to or greater than the aromatic portion. The level of aromatics that is consequently reported by the analyst is therefore dependent on the technique used.

A large number of methods are available for the determination of aromatics in petroleum distillates. Many of the methods have been formalized as IP and/or ASTM standards and are based on one of the following techniques:

- Chromatography (gas, liquid and supercritical fluid)
- Mass spectrometry
- Spectroscopy (nuclear magnetic resonance, ultraviolet and infrared)

The complexity of both the methods and instrumentation vary considerably as do the precision and cost of analysis. The absence of a cost-effective reliable and precise method has led to considerable activity, on both sides of the Atlantic, towards the development of alternative procedures.

Two chromatographic methods are currently favoured for the determination of per cent mass (or volume) aromatics in diesel fuel. IP391/90 is an established liquid chromatographic method widely used throughout Europe. CEN/TC19/WG18 has recommended a number of modifications to this method, most notably the inclusion of a column backflush step to elute the polycyclic aromatic hydrocarbons (PAHs), which will significantly improve the precision of the method and widen its scope. Supercritical fluid chromatography (SFC) is the preferred technique in the US with the recently published ASTM D5186 method of test. Although ASTM D5186 offers a very practical solution to the problem of measuring diesel aromatic content, the SFC method is less versatile, less robust and less cost-effective than the IP391 liquid chromatographic procedure.

This document summarizes the various analytical procedures that are currently available for the determination of diesel fuel 'aromaticity'.

2. DEFINITION OF AROMATICS

There are two common measures of aromaticity - aromatic hydrocarbon content and aromatic carbon content - which are defined as follows:-

Aromatic hydrocarbon content:- is defined as the mass (or volume) per cent fraction of the sample which contains only molecules having at least one aromatic ring structure. It is usually determined by a chromatographic or mass spectrometric (MS) technique.

Aromatic carbon content:- is defined as the mole per cent of carbon in the sample which is present as part of an aromatic ring structure (%CA). It can be determined directly by carbon-13 nuclear magnetic resonance (NMR) and, indirectly, by proton NMR, infrared (IR) spectroscopy and the empirical n-d-M method (ASTM D3238).

Note:
The n-d-M method (ASTM D3238) is a structure-property correlation using a relationship between density (d), refractive index (n) and molecular weight (M) to calculate the %CA. All three parameters can be measured or determined using standard product inspection data (e.g. M can be estimated from viscosity or GC simulated distillation data).

3. DISCUSSION

A summary of analytical methods used to determine the 'aromaticity' of petroleum middle/vacuum distillates is given in **Table 1**. Some of the listed methods do not include diesel fuels within their scope and it is usually necessary to make some modifications in order to encompass the diesel fuel boiling range.

3.1. ANALYTICAL METHODS AND TECHNIQUES

Of the thirteen tabulated methods, six use some form of chromatography, four use mass spectrometry (MS), two use a spectroscopic technique and one employs an empirical relationship (the n-d-M method).

Two techniques which are not included in the table but merit consideration are infrared spectroscopy (e.g. Brandes method) and liquid chromatography-gas chromatography (LC-GC). The former method estimates %CA and ideally needs to be calibrated against a large number, and variety, of sample-types (i.e. straight-run, catalytically-cracked, hydrotreated, visbroken, etc.) to make it universally applicable. CEN/TC19/WG18 is working on such an approach using carbon-13 NMR data, combined with factor analysis, to calibrate the infrared method. (note: the n-d-M calculation has been discounted by CEN/TC19/WG18 because of its poorer precision and accuracy compared with the 13C-NMR method, e.g. IP392). The LC-GC method can be operated as a directly coupled technique (on-line) but in practice is still, more commonly, performed off-line.

3.2. AROMATIC DATA (TYPES AND UNITS)

Carbon-13 and proton NMR (IP392/90), infrared and the n-d-M method (ASTM D3238) measure the aromaticity of the sample as mole per cent aromatic carbon. No differentiation is given between the types of aromatic species (e.g. alkylbenzenes, alkylnaphthalenes, etc.) present.

Chromatographic methods which involve a preparative separation of the saturated and aromatic hydrocarbons followed by off-line gravimetric determination of the two fractions (ASTM D2549, D2007 and IP 368/90) provide a measurement of the mass% total aromatic hydrocarbon content. On-line detection (IP391/90, ASTM D5186) reduces the analysis time and offers automation. The classical FIA method (ASTM D1319/IP156) yields vol% total aromatics while calibrated methods such as IP391/90 can provide either mass% or vol% data. At present only IP391 determines aromatic-type information (i.e. mono-aromatics, di-aromatics and poly-aromatics) although ASTM D5186 has the potential to provide these data too. CEN/TC19/WG18 has modified the IP391 method to include a column backflush after the di-aromatics; this change will enhance the detection limit for PAHs (down to 0.01% mass) as well as improve the overall precision of the method.

MS methods fall into two camps; those which require a pre-separation of the saturated and aromatic hydrocarbons versus those which do not. The two ASTM methods which include diesel fuel within their scope (D2425, D3239) both require the pre-separation. These methods, therefore, use the chromatographic data to yield the % total aromatic hydrocarbon content and the MS data to provide information on the types of aromatics present. Most petroleum laboratories, however, use either low (e.g. 9X9, 12X12, etc.) or high (e.g. 19X19, 22X22, etc.) resolution matrix methods, originally developed by Gallegos, to analyse the total sample directly. Such methods can be calibrated to give either mass% or vol%

data and provide data on both the total hydrocarbon aromatic content and the types of aromatics present.

The Burdett UV method determines the mole per cent of mono-, di- and tri-aromatics which is then converted to mass% using the sample's number average molecular weight (MWt) value.

3.3. SCOPE OF THE METHOD

The main criterion here is the boiling range of the sample. Techniques and methods developed for lower boiling samples, e.g. gasolines, may be more difficult to adapt than those developed for the higher boiling samples (e.g. vacuum gas oils).

3.4. SAMPLE PRE-TREATMENT

A majority of the methods listed in **Table 1** require no sample pre-treatment apart from dilution of the diesel fuel in an appropriate solvent. ASTM D2425 and D3239 require isolation of the aromatics fraction prior to MS analysis.

The Burdett UV method requires a sample MWt value; however, for a specific boiling range product such as diesel fuel it would be practical to use a typical or average value.

3.5. ANALYSIS TIME

The time of analysis can depend on a number of factors such as the sample frequency, competence/training of the analyst, degree of automation, etc. MS analyses, for example, will be performed one at a time whilst the chromatographic analyses may be run either in parallel (ASTM D1319, D2549, D2007) or as a batch on an autosampler (IP391, ASTM D5186). An estimate of the elapsed analysis time is given in **Table 1**.

3.6. ACCURACY AND PRECISION

The accuracy of a method is defined as its ability to determine the real value of the measured parameter. Thus IP392/90 (carbon-13 NMR) should be the most accurate method for aromatic carbon content because it measures this parameter directly. Infrared, proton NMR and n-d-M are less accurate because they are indirect methods requiring calibration/calculation.

IP368/90 should be the most accurate method for measuring mass% aromatic hydrocarbon.content because it determines the mass% value by gravimetry. Note that IP368, IP391 and ASTM D5186 are expected to give a more accurate saturates/aromatics separation because they utilize a detector to identify the separation point. However, IP391 and ASTM D5186 do not determine mass% concentrations directly but utilize a calibration algorithm (albeit a very simple one in the case of D5186). Other chromatographic methods (D2549, D2007) are less accurate because the separation quality is not monitored by an in-line detector.

All MS methods are calibrated against a chromatographic method (for total aromatic hydrocarbon content) and against various model compounds (for aromatic-type data). A much higher degree of skill/training is required to operate the instrument and interpret MS data.

Precision is defined as the repeatability (*intra*-laboratory) and reproducibility (*inter*-laboratory) of the method established by round robin testing. For a universal method, reproducibility is the more important of the two measures of precision. The precision of ASTM and IP methods will be stated in the test procedure although it is not always possible to compare one method with another because of differences in the sample-types and statistical analysis used to determine the precision. It is important to remember that an accurate method can be imprecise and a precise method can be inaccurate!

Defining the absolute or relative accuracy/precision of a method is a difficult task. For example, it is of little practical value having a precise accurate method if it is only applicable to a limited sample-type such as straight-run gas oils. One factor which must be considered is the presence of interferents. Thus, carbon-13 NMR cannot differentiate between aromatic and olefinic carbons and hence its accuracy will be poorer for cracked (e.g. cycle oils, coker gas oils, etc.) products. Similarly, organosulphur compounds co-elute with the aromatics in the chromatographic methods and will therefore be included in the aromatic content. Many of the methods do not measure polar components but normalize the saturate and aromatic contents to 100% of the sample; the accuracy of such methods will be reduced for samples with a significant polar content.

The accuracy and precision for the methods listed in **Table 1** have been classified either as poor or good. 'Poor' indicates an accuracy or reproducibility of >10% relative for diesel fuels with 20-35% mass aromatic hydrocarbon content (equivalent to about 10-20 mole% CA). 'Good' signifies an accuracy or reproducibility of <5% relative for the same aromaticity [Note: individual laboratories may classify the accuracy/precision of these methods slightly differently, depending on their expertise/experience].

3.7. SUITABILITY FOR REFINERY USE

Whether a method is suitable for refinery use depends mainly on the legislative/specification aspects of the sample. If there is only one approved standard method then the cost of instrumentation and analysis assumes a lesser importance. Ideally there should be a choice of methods available.

Suitability for refinery use then comes down to the cost of instrumentation and the ease of analysis (e.g. whether a skilled technician is required, ability to automate the method, etc.). MS and NMR methods are not therefore considered suitable for refinery use at the present time. All other methods are suitable and the choice will depend on the type of data required, the accuracy/precision expected and availability of instrumentation.

3.8. GENERAL COMMENTS

ASTM D1319 - laborious method which has been shown to be unreliable for diesel fuels (heated FIA)

ASTM D2789 - test method for low olefinic gasolines

ASTM D2425 - widely used throughout the industry; matrix methods do not require pre-separation; problems with some samples (e.g. cracked and hydrotreated products, high sulphur samples)

Burdett Method - cheap and simple method but imprecise

ASTM D5186 - new method and technique chosen by ASTM to 'replace' FIA (D1319) for the determination of aromatic hydrocarbon content in diesel fuels. Instrumentation is expensive and still not widely available in Europe. Measures only total aromatic hydrocarbon content and not aromatic-types. Scope of the method covers aromatic contents from 5-75% mass.

IP392 - proton and carbon-13 NMR standard

IP391 - best option as cost-effective routine method for measuring aromatic totals and types! Addition of a backflush option should improve precision and enable the quantification of low levels of PAHs.

ASTM D3239 - replaced by matrix methods (e.g. 19X19)

19X19 - overcomes some of the problems associated with low resolution MS methods such as D2425

ASTM D2549 - obsolete

ASTM D2007 - obsolete

IP368 - developed for lubricant base oils but easily adapted to diesel fuels by changing the mobile phase to pentane (note: samples with low IBP may lose the most volatile components in the work-up). Laborious but could be automated at cost!

ASTM D3238 - standard method and cost-effective because it utilizes routine product inspection parameters. Doubts about the reproducibility. Method likely to be superceded by NMR and IR procedures.

Infrared %CA - potential for rapid and cost-effective determination of

LC-GC - would benefit from availability of automated on-line LC-GC instruments.

4. CONCLUSIONS

Laboratories will have different requirements and facilities and therefore it is important to have a suite of analytical techniques/methods available. The choice of method, whether for legislation, specification or general information purposes, must consider a number of factors:-

(a) Is % mass, % volume, or %CA information required?

(b) Is information on the different aromatic-types required?

(c) What interferents are allowable/not allowable?

(d) Is the method suitable for a wide range of sample types (e.g. straight-run, cracked and hydrotreated products)?

(e) What degree of precision/accuracy is required?

(f) Which laboratories are expected to perform the analysis?

(g) What is the scope (e.g. boiling range, blended diesel fuels versus diesel fuel blending components) of the method?

(h) Are any other data, e.g. saturate-type analysis, required?

By identifying the key points and requirements it will be possible to eliminate inappropriate methods and focus on the most promising procedures. Subject to these considerations, the following general conclusions can be drawn:

- Mass spectrometric methods provide the most detailed analysis of hydrocarbon-types in middle distillates but are not considered suitable for every day refinery use.

- Classical chromatography methods (D1319, D2007, etc.) have been superceded by high performance liquid chromatographic (HPLC) techniques (IP368, IP391).

- ASTM D5186 (SFC) and IP391 (HPLC) are the most attractive options at the present time. HPLC is a more established technique than SFC as well as offering total and aromatic-type compositional data. IP368 offers a cheap and practical alternative for small laboratories.

- %CA is best determined by carbon-13 NMR but this will not be practical for most laboratories. Correlations with infrared data offer a lower cost alternative.

5. RECOMMENDATIONS

From an analytical standpoint, there is little to choose between the IP391 and ASTM D5186 methods for the determination of total aromatic hydrocarbon content. Both methods provide an accurate measurement of the % mass aromatic hydrocarbon content. IP391 is the more versatile method since it is capable of determining aromatic-types (mono-aromatics, di-aromatics and PAHs), as well as total aromatics, either as volume % or mass %. Members of CEN/TC19/WG18 overwhelmingly expressed a preference for methods which differentiated between the aromatic hydrocarbons. Therefore, a diesel specification for total aromatics could refer to both IP391 (or its modified version with backflush) and ASTM D5186. However, only the former is appropriate where the specification refers to any limit on certain aromatic-types (e.g. PAHs).

Carbon-13 NMR is the analytical method of choice for the determination of CA, although infrared techniques offer a more cost-effective method for routine analysis.

Table 1 Analytical methods used to determine the'aromaticity' of petroleum middle/vacuum distillates .

METHOD	ANALYTICAL TECHNIQUE	AROMATIC MEASURED	UNITS	BOILING RANGE	SAMPLE PRETREATMENT	ANALYSIS TIME (HOURS)	PRECISION	ACCURACY	SUITABILITY FOR USE
ASTM D1319/X9 (HA)	ADSORPTION CHROMATOGRAPH	TOTALS	% VOL.	< 315°C < 600°F	NONE	3-8	POOR (VERY OPERATOR DEPENDENT)	POOR FOR DIESELS	YES
ASTM D2789/86	LOW RESOLUTION MASS	TOTALS & TYPES	% VOL.	< 210°C < 411°F	NONE	1-3	GOOD	GOOD	NO
ASTM D2425 9 X 9 MATRIX	LOW RESOLUTION MASS SPECTROMETRY	TOTALS & TYPES	% MASS OR % VOL.	200-300°C 392-662°F	NONE	1-3	GOOD	GOOD	NO
BURDETT METHOD	ULTRAVIOLET SPECTROSCOPY (UV)	TOTALS & TYPES	% MOLE OR % WT	350-350°C 662-1022°F	FOR % WT NEED MWI BY OSMOMETRY	1-3	GOOD	GOOD	YES
ASTM D5186	SUPERCRITICAL CHROMATOGRAPH	TOTALS	% MASS	200-400°C 392-752°F	NONE	1-3	GOOD	GOOD	POSSIBLY
IP 392/90	NUCLEAR RESONANCE SPECTROSCOPY	TOTALS	% C_A	200-550°C 392-1022°F	NONE	1-3	GOOD	GOOD	NO
IP 391/90	HIGH LIQUID CHROMATOGRAPH	TOTALS & TYPES	% VOL. OR % MASS	50-400°C 122-572°F	NONE	1-3	GOOD	GOOD	YES
ASTM D 3239/86	LOW RESOLUTION MASS SPECTROMETRY	TYPES	% VOL.	200-538°C 392-1000°F	ISOLATION OF AROMATICS	3-8	D2425	D2425	NO
19 X 19 MATRIX METHOD	HIGH RESOLUTION MASS SPECTROMETRY	TYPES	% MASS OR % VOL.	350-509°C 662-948°F	NONE	1-3	GOOD	GOOD	NO
ASTM D2549/85	OPEN COLUMN PREPARATIVE CHROMATOGRAPH	TOTALS	% MASS	232-538°C 450-1000°F	NONE	> 1 DAY	GOOD	POOR	YES
ASTM D2007/86	PREPARATIVE CHROMATOGRAPH	TOTALS	% MASS	> 260°C > 500°F	NONE	3-8	GOOD	POOR	YES
IP 368/90	PREPARATIVE CHROMATOGRAPH	TOTALS	% MASS	> 270°C > 500°F	NONE	3-8	GOOD	GOOD	YES
ASTM D3238 (n-d-M)	CALCULATION BASED ON ANALYTICAL DATA	TOTALS	% C_A	200-550°C 392-1022°F	DENSITY (d) REFRACTIVE INDEX MOL. WT (M)	3-8	GOD	GOOD	YES