

A Comparison of Ten Different Methods for the Analysis of Saturates, Olefins, Benzene, Total Aromatics, and Oxygenates in Finished Gasolines

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Abstract

The Technical Committee 19 of the European Committee for Standardization (CEN/TC19) in the "Lisbon resolution" requested to evaluate replacement methods to the fluorescent indicator absorption (FIA) (American Standardization for Testing and Material D 1319) method for the determination of aromatics and olefins in gasolines. In the same resolution it was requested to review the two existing methods for the determination of benzene content of gasolines, anticipating lower limit values in future European gasoline specifications. As a result of this request, a round robin (RR) was organized in which 8 gasoline samples are analyzed using 10 different methods in 33 laboratories. The methods used in the RR include, apart from the FIA method, one-dimensional gas chromatography (GC) and multidimensional GC, with and without specific detectors and spectroscopic analysis methods. This study describes these methods in short, gives an evaluation of the results of the RR, and draws a conclusion on the outcome.

Introduction

During the last decade, gasolines have been subject to an important change in composition. Benzene and some other aromatic compounds are classified as toxic air pollutants under the legislation that exists in different countries. The U.S. Clean Air Act of 1990 mandates the reformulation of gasoline, aimed at reduction of the emissions of toxic compounds from combustion engines. In view of the requirements formulated by the Environment Protection Agency (EPA), a quantitative determination of benzene concentrations at all process stages is essential to meet the target values and achieve optimum control of the refining and blending processes. Similar legislation is pending in other countries. The pollutant limits and corresponding test methods from the Clean Air Act may be expected to serve as

guidelines in other jurisdictions. In the United States, the EPA regulations specify the level of benzene not to exceed 1% (v/v). Even more stringent regulations exist in Europe. Table I gives an overview of the changing European gasoline specifications with time. In an attempt to replace the lead compounds and reduce the aromatics and sulfur content for reduction of pollution and still satisfy the combustion properties, several different refinery process streams are combined. These reformulated gasolines may now contain straight run naphtha, fluid catalytically cracked naphtha, reformate, alkylate, isomerate, hydrocrackate, and oxygenates such as methyl-tert-butyl ether (MTBE), tert-amylmethyl ether (TAME), ethyl-tert-butyl ether (ETBE), ethanol (ETOH), and higher alcohols.

The analyses of hydrocarbon-types present in different oil fractions have been the subject of many investigations in the past. All of the methods described for these analyses, being chromatographic or spectroscopic, produce different results with different precision. The most frequently used method, which is still specified by various legislation and standardization authorities for the analysis of hydrocarbon types in gasoline is the fluorescent indicator absorption (FIA) method as described in American Standardization for Testing and Materials (ASTM) D1319 (1). In view of the limited scope and rather wide precision bias of the method and the problems arising from gasoline samples con-

Table I. The Changing Gasoline Specifications in Europe

			1993	2000	2005	2008
Lead	g/L	max.	0.013	none	none	none
Benzene	%(v/v)	max.	–	1	1	review
Oxygen	%(m/m)	max.	–	2.7	2.7	review
Aromatics	%(v/v)	max.	–	42	35	review
Olefins	%(v/v)	max.	–	18	18	review
Sulfur	mg/kg	max.	500	150	50	10

taining oxygenates, the Technical Committee of the European Committee for Standardization (CEN/TC19) has requested the evaluation of replacement methods for the FIA method. The reason for this is the recently formulated obligation of CEN TC19 in connection with the changed policy for dating test methods in relation to the European Commission's fuel directive. They also requested, as one additional work item, to review the two existing methods for the determination of benzene content, namely European Normalization (EN) 238 (2) and EN 12177 (3). The applicability of these standards shall be determined anticipating lower limit values in the future, taking into account that the limiting value should not be smaller than two times the reproducibility of the related test method.

They selected nine potential candidate methods for replacing the FIA method and the method for the determination of benzene. A prerequisite for replacement was that the candidate method should provide results comparable with those of the FIA method and that the precision should be significantly better.

The FIA method and the nine potential candidate methods together with the comparable American methods (as a reference) are listed in Table II and discussed in the Experimental section. This paper describes the results of a round robin (RR) of the analyses of eight gasoline samples by a large number of European laboratories, including several American laboratories.

Experimental

It was stressed to the participants of the RR that no variations or modifications of whatever kind should be made to the methods listed. It was felt that it is absolutely necessary to adhere exactly to the provisions given in the written test method. Also, using any other method than those listed would disqualify the lab and its results.

Analysis methods

Method A. Determination of total aromatics, total olefins, oxygen compounds, and benzene in finished petrol. Gas chromatographic analysis by column switching procedure (reformulyzer) according to prEN 14157 (4) and ASTM D6839-02 (5)

This multidimensional gas chromatographic (GC) analysis system is based on the well-known PIONA concept (paraffins, isoparaffins, olefins, naphthenes, and aromatics), described in the literature (6). It performs all the tasks of the PNA (paraffins, naphthenes, and aromatics) and PIONA analyzers and more. The system determines all hydrocarbon types: paraffins, isoparaffins, olefins, naphthenes, and aromatics in finished gasolines and gasoline-related streams. In addition this system is extended to quantitate oxygenates in reformulated gasoline.

A typical sequence is, for example, the first the alcohols and higher-boiling aromatics are absorbed in a trap (sulfate column I). The remaining aromatics are separated from the other

components by means of a polar column (OV275). The ethers are separated from the remaining fraction by means of another trap (sulfate column II). The olefins are separated from the saturated compounds by an olefin trap (silver salt) in two steps. This is necessary because of the limited capacity of such traps for high amounts of butenes and high total olefin contents. Permitting trap capacity and olefin concentration, the separation can be performed in one step. Next the remaining saturated hydrocarbons are separated into paraffins and naphthenes according to their carbon atom number using a 13 \times column. The ethers are then eluted from the sulfate column II and separated and detected according to boiling point. The olefins are desorbed from the olefin-trap and hydrogenated in a Pt-reactor. They are separated and detected as the corresponding saturated compounds using the 13 \times column. The alcohols and higher-boiling aromatics are eluted from the OV275 and sulfate I column and separated and detected according to boiling point. By the use of the corresponding flame ionization detector (FID) response factors the mass distributions of the groups can be calculated, following the internal normalization method. For samples containing oxygenates that cannot be determined by this method, the hydrocarbons are normalized to 100% minus the value of oxygenates as determined by other methods. The results in % (m/m) are converted to % (v/v) by application of density factors. The resulting chromatogram of such a separation is depicted in Figure 1.

Method B. The determination of benzene and total aromatics and benzene by GC using column switching, according to Deutsche Industrie Norm (DIN) 51413-9 (7)

The benzene containing fraction and other aromatic compounds are isolated from the injected sample using a polar high-resolution capillary column (1,2,3-tris(2'-cyanoethoxy-propane) or polyethylene-glycol). These fractions are further separated on a second, nonpolar capillary column (polymethyl-phenyl-siloxane). By the use of the corresponding FID response factors the mass distributions of the aromatics peaks can be calculated by comparison with an internal standard [preferably methyl-isobutyl-ketone (MIBK)]. The results in % (m/m) are converted to % (v/v) by application of density factors.

Table II. Methods Used in the Round Robin

	Method	Technique	Comparably	Aromatics	Olefins	Benzene	Oxygenates
A	prEN 14517	MDGC/ reformulyzer	ASTM D 6839	Y	Y	Y	Y
B	DIN 51413-9	MDGC	ASTM D 5580	Y	N	Y	*
C	ASTM D1319	FIA		Y	Y	N	N
D	NF M 07-086	1D-GC	ASTM D 6733	Y	Y	N	*
E	EN 238	IR spectroscopy		N	N	Y	N
E2	EN 238 mod.	IR spectroscopy		N	N	Y	N
F	EN 12177	MDGC	ASTM D 3606	N	N	Y	*
G	EN 1601	1D-GC/O-FID	ASTM D 5599	N	N	N	Y
H	EN 13132	MDGC	ASTM D 4815	N	N	*	Y
K	NF M 07-094	1D-GC (Octyl.)		Y	N	Y	*

* Not included in the method but, in principle, possible (development necessary).

Method C. The determination of hydrocarbon types with FIA according to ASTM D1319-95* (1)

In the FIA method hydrocarbon samples are separated using a special glass adsorption column packed with activated silica gel and a small layer of fluorescent indicator dyed gel. Pressurized isopropyl alcohol (IPA) promotes the vertical migration of the sample down the column (open column liquid chromatography). The dyes are also separated selectively with the hydrocarbon types, which differentiate the boundaries of the saturate, aromatic and olefinic fraction under UV light. The separated bands are measured after visual inspection. The FIA method identifies saturates, nonaromatic olefins, and aromatics up to a boiling point of 315°C. Results are reported in % (v/v).

The scope of the method defines the limits of the aromatics to 5–99% (v/v) and the olefins to 0.3–55% (v/v). The limit of the final boiling point is set to 315°C.

(* This method, in contrast with newer issues, prescribes that deparaffinization of the sample is optional. In the European gasoline specification EN 228 it is mentioned not to deparaffinize the samples.)

Method D. Determination of hydrocarbon group type contents in motor gasolines from detailed analysis—method by capillary GC according to Norme Française (NF) M 07-086 (8)

This method utilizes a single high-resolution nonpolar capillary column (polydimethylsiloxane) to separate all individual compounds. Each peak is identified by comparing its retention time with a table of reference retention times and by visual matching with a standard chromatogram or by a specific software program. By the use of the corresponding FID response factors, the mass distributions of the compounds can be calculated, following the internal normalization method. The results in % (m/m) are converted to % (v/v) by application of density factors.

Method E. The determination of the benzene content of petrol by IR spectrometry according to EN 238 (2)

The sample is diluted with cyclohexane and an infrared spectrum is recorded in the mid-infrared region, namely from 730 to 630 cm^{-1} . The absorbance is measured at 673 cm^{-1} and compared with the absorbance of standard benzene solutions. The benzene content is then given in g/100 mL and converted to % (v/v) by application of density factors. The scope of the method defines the limits of benzene to 0.1–20% (v/v).

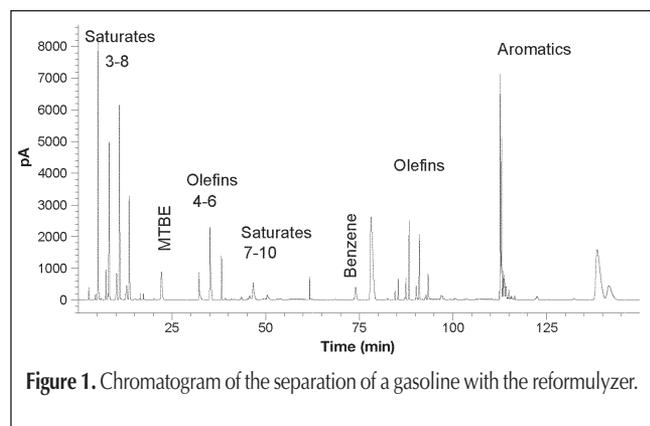


Figure 1. Chromatogram of the separation of a gasoline with the reformulyzer.

Method E2. The determination of the benzene content of petrol by IR spectrometry according to EN 238 mod. (9)

The sample is diluted with cyclohexane and an IR spectrum is recorded in the mid-IR region, namely from 730 to 630 cm^{-1} . The absorbance is measured at the maximum of the peak located near 673 cm^{-1} and compared with the absorbance of standard benzene and toluene solutions. The benzene content is then given in g/100 mL and converted to % (v/v) by application of density factors. The scope of the method defines the limits of benzene to 0.2–3.0% (v/v).

Method F. The determination of benzene content of unleaded gasoline by GC according to EN 12177 (3)

The benzene-containing fraction is isolated from the injected sample using a first capillary column in a multidimensional GC. The isolated fraction is further separated on a second capillary column with a different polarity [note: the polarity of the columns is defined only by the required minimum resolution between benzene and the matrix in the second (nonpolar) column]. By the use of the corresponding FID response factors the mass concentration of the benzene peak can be calculated by comparison with an internal standard (preferably MIBK). The results in % (m/m) are converted to % (v/v) by application of density factors. The scope of the method defines the limits of benzene to 0.05–6.0% (v/v) and the final boiling point of the sample to 220°C.

Method G. The determination of oxygenated compounds and total organically bound oxygen content by GC and oxygen-selective detection (O-FID) according to EN 1601 (10)

After separation of the sample using a capillary column, the organic oxygenate compounds are selectively converted to carbon monoxide, hydrogen, and carbon in a pyrolytic cracking reactor. In a hydrogenation reactor, carbon monoxide is then converted to methane and subsequently detected using an FID (O-FID). The mass concentration of the individual oxygenates is determined by comparing their peak areas with an internal standard (an alcohol or ether that is not present in the sample). The results in % (m/m) are converted to % (v/v) by application of density factors. The scope of the method defines the limits of individual organic oxygenate compounds to 0.17–1.5% (m/m), total organically bound oxygen to 3.7% (m/m) in unleaded gasoline having a final boiling point not greater than 220°C.

Method H. The determination of organic oxygenate compounds and total organically bound oxygen content by GC using column switching according to EN 13132 (11)

The oxygen-containing compounds are isolated from the sample using a first capillary column in a multidimensional GC. The isolated fraction is further separated on a second capillary column with a different polarity [note: the polarity of the columns is defined only by the required minimum resolution between two components to be determined in the second (nonpolar) column]. Each oxygenate peak is identified by comparing its retention time to a table of reference retention times and by visual matching with a standard chromatogram. By the use of the corresponding FID response factors, the mass distributions of the compounds can be calculated using an internal standard. The results in % (m/m) are converted to % (v/v) by application of density factors.

The scope of the method is 0.17–15% (m/m) individual and organically bound oxygen up to 3.7% (m/m).

Method K. Determination of benzene, toluene, and MTBE in petrol—method by capillary GC according to NF M 07-094 (12)

This method utilizes a single high-resolution nonpolar capillary column (a bonded methylsilyloxane) to separate all individual compounds. Each peak is identified by comparing its retention time with a table of reference retention times and by visual matching with a standard chromatogram. By the use of the corresponding FID response factors the mass distributions of the compounds can be calculated by using an internal standard (butanone). The results in % (m/m) are converted to % (v/v) by application of density factors.

Utilized samples

Eight gasoline samples were selected according to the following criteria: aromatics between 18% and 46% (v/v); olefins between 1% and 27% (v/v); benzene between 0.05% and 1.5% (v/v); and the oxygenates ETOH, MTBE, ETBE, and TAME. Only four samples contained oxygenates.

They were sampled and shipped in sealed vials to the participating laboratories and stored under refrigeration. After reconditioning in the sealed vials to the appropriate sampling temperature, they were subsampled and analyzed in duplicate, without dilution.

Analysis protocols to which the participants had to adhere strictly were defined. These included sample handling, the use of calibration samples and methods (if appropriate), and experimental conditions as described within the analysis methods. Results were reported both by weight and volume to two decimal places.

Results and Discussion

Out of the total of 78 nominated laboratories, a variety of parties participated with the different analysis methods and provided results. This is tabulated in Table III. The disadvantages, shortcomings and problems involved in the various methods are briefly discussed in the next section.

Table III. Nominated and Participating Laboratories

Method code	Aromatics	Olefins	Benzene	Oxygenates	Nominated	Results
A	X	X	X	X	28	25
B	X		X		15	9
C	X	X			33	23
D	X	X			11	6
E			X		14	6
E2			X		17	8
F			X		16	8
G				X	17	8
H			X		10	2
K		X			12	5

Method A

The time-consuming analysis had a total analysis time of 150 min. The method, although fully automated, requires an experienced and trained analyst who is familiar with both the method and the instrument to interpret the chromatogram.

Method B

Nonaromatic hydrocarbons with high boiling points may coelute with the aromatic fractions on the first column and subsequently be transferred to the second column, and may thus be incorporated in the total of the higher boiling aromatic compounds. Some polar oxygenated compounds present in the sample, predominantly alcohols and ethers, will also be transferred together with the aromatics fractions to the second column. By using an appropriate temperature program for the two columns, the elution of these compounds can be optimized so that they will not interfere with the quantitation of the aromatics.

Method C

A number of potential sources of error exist in the FIA method. When the different hydrocarbon types separate, the zone boundaries are often not sharp, and the hydrocarbon types partially overlap, which leads to errors in interpreting the data. Samples containing light hydrocarbons require depentanization, which may cause the loss of C₆ compounds and lead to inaccuracies (13,14). Therefore it was decided for this RR not to depentanize the samples. Oxygenated compounds may interfere with the separation [i.e., ethers may produce double zone boundaries and alcohols (especially those more polar than IPA) migrate slower than the mobile phase]. And finally, human error is an important factor, because the determination of the different separated bands is done by visual means. Improper packing of the silica gel or incomplete elution of hydrocarbons by the mobile phase also leads to erroneous results.

Method D

Although a high resolution column has a high resolving power and a high peak capacity, an important source of error in this method is coelution of compounds of different classes. It is apparent that there is ample overlap of peaks of different classes, especially if the sample contains relative high concentrations of olefins. The method already incorporates this by mentioning the possible coelution of benzene with methylcyclopentene and toluene with 2,3,3-trimethylpentane. Time-consuming analysis (total analysis time for a sample with FBP = 220°C is over 2 h).

Method E

The presence of cyclopentadiene in the sample will cause an interference with the determination of benzene when it exceeds 5% (v/v). A labor-intensive and intelligent selection of model mixtures is needed for calibration.

Method E2

The presence of cyclopentadiene in the sample will cause an interference with the determination

of benzene when it exceeds 5% (v/v). The presence of ether (ETBE, MTBE, or TAME) has only a dilution effect on the results obtained. No interference by other compounds has been detected. A labor-intensive and intelligent selection of model mixtures is needed for calibration.

Results of the RR, specified per method

Method A (DIN 51448-2 reformulyzer)

Twenty-five laboratories submitted results. The precision in this RR was better than reported in the method ASTM D1319. The means were in good agreement with FIA. The exception was that the samples containing butane were a little higher in aromatics than FIA but agreed between GC methods. It was agreed that this effect was a result of the requirement from EN 228—not to depentanize the samples, although the official FIA method would in these cases request a depentanization (see Figures 2–4).

Method B (EN 12177 with extension for total aromatics)

Ten laboratories submitted results. The means were in good agreement with FIA. Lab 10 had results 2% low in all cases. These were not identified by Hawkins (15), so there was no clear indication whether these results should be eliminated.

Method D (NF M 07/086 detailed hydrocarbon analysis)

Only eight laboratories submitted results and only six labs sent duplicate results. The two labs with only single results were excluded from the RR calculation, but their results will be listed in the RR report. No Hawkins (15) outliers were found because of the small sample set. One Cochran (15) outlier was identified (see Figures 2 and 3).

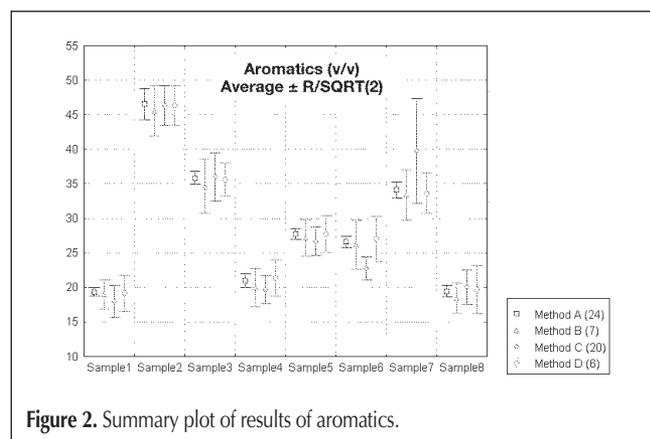


Figure 2. Summary plot of results of aromatics.

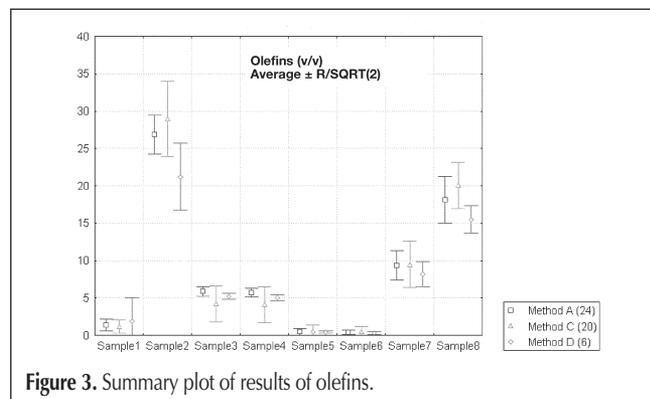


Figure 3. Summary plot of results of olefins.

Methods E (EN 238 IR spectroscopy) and E2 (IR modified)

The method had been modified by some French laboratories to give an improved precision. There were six labs using EN 238 and eight using the modified method. Both the E and E2 methods agreed with the means of all the other benzene methods. The precision was lower than stated in EN 238 for samples containing < 1% benzene, but these differences were not judged to be very significant (see Figure 4).

Method F (EN 12177)

In general the precision was better than Method E. Method F is very similar to Method B. Method F is also the current reference method for benzene determination in EN 228 (see Figure 4).

Method K (NF M07/094)

Precision was not as good as Method F. The range plots for the methods showed that the mean values were all very similar (see also Figure 4).

Conclusion

As a result of detailed discussions, the organizing working group came to the following conclusions and recommendations concerning the FIA replacement candidates: (a) From the precision viewpoint, method A was clearly the most preferable candidate. The method enabled the determination of not only total aromatics and olefins as requested, but it had the additional benefit that benzene and oxygenates can be measured with good precision. Because the method can, from internal data, produce much more detail than is shown in the current method description, it is felt that method A is also fit for possible additional future requirements.

(b) For method B, the organizing working group concluded that more analytical work is needed for improving analytical performance. The precision results for method B, which can at this stage only determine total aromatics and benzene, did not turn out to be as good as could be expected from the previous German experiences; the means compared well with both method A and C. First analytical improvements had already been identified.

(c) For method D, the organizing working group concluded that more analytical work is needed for improving analytical details. This method displayed, in comparison with the other

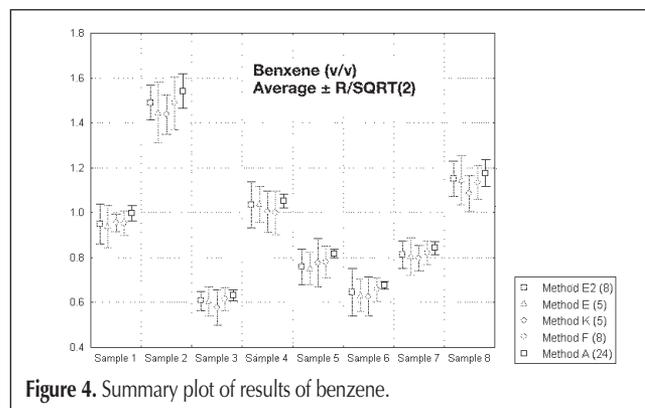


Figure 4. Summary plot of results of benzene.

methods, a tendency towards lower olefin contents when samples with higher olefin content were analyzed. Also here, experts were already working on analytical improvement.

(d) As for the results for the benzene contents methods, from the precision viewpoint, method A was once again the most preferable method for benzene determination. When comparing the means, it was concluded that all methods were in excellent agreement. It must be noted, however, that both methods B and D need further work for analytical improvement, so these are not recommended at this point as a primary choice for benzene determination. One more problem lies in the rather small number of labs, so some of these results may not be totally valid or representative. The two IR methods (E, E2) both agreed very well with the results obtained from the GC methods. Although some small improvements concerning precision have been observed, the experts felt that these should not be judged to be very significant when looking at the disappointingly low number of participating labs.

As a consequence, method A was the most preferable candidate that can be proposed as a replacement for the FIA method. It is also worth mentioning that the results from the RR exercise clearly displayed a defect of the FIA method, when samples containing significant amounts of C₅ and lighter were analyzed without deparaffinization.

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