

State of California
California Environmental Protection Agency
Air Resources Board

STAFF REPORT: INITIAL STATEMENT OF REASONS FOR PROPOSED RULEMAKING

PUBLIC HEARING TO CONSIDER AMENDING THE TEST METHODS DESIGNATED FOR
DETERMINING THE BENZENE, AROMATIC HYDROCARBON, OLEFIN, AND SULFUR
CONTENT OF PHASE 2 GASOLINE

I. INTRODUCTION

We are proposing that the Air Resources Board (ARB or Board) amend its designation of the test methods used to measure the amount of benzene, aromatic hydrocarbons, olefins, and sulfur in gasoline. The updated methods would be used to determine if motor vehicle gasoline complies with the ARB's Phase 2 reformulated gasoline (RFG) requirements.

The Board adopted the Phase 2 RFG regulations in November 1991 with an effective date of March 1, 1996. The Phase 2 RFG specifications include limits for benzene, aromatics, olefins, and sulfur. (13 CCR section 2262.2 et seq.) The test methods for determining compliance with these limits are specified in section 2263(b), title 13, California Code of Regulations.

Although the currently specified test methods were the best procedures available when the RFG 2 regulations were adopted, both the ARB and the affected industry recognized that they had shortcomings, especially in terms of precision. Accordingly, in adopting the regulations, the Board directed staff to work with industry to identify improved test procedures.

To this end, we have conducted in-house evaluations of various test methods, participated in interlaboratory studies of test method precision carried out by the American Society of Testing and Materials (ASTM), and met regularly with members of the Western States Petroleum Association (WSPA) to discuss test methods development. We also held two workshops which were attended by members of the oil industry, instrument manufacturers, and other interested parties. Through these efforts, we have identified new and updated test methods for benzene, aromatic hydrocarbon, olefin, and sulfur content. These improved test methods are more precise and, in some cases, more accurate than the methods currently designated by the ARB. Generally, the test methods we propose reflect the consensus of the participants in this process. The proposed changes are set out in Table 1.

Table 1. Proposed Test Method Changes

<u>Regulated Component</u>	<u>Currently Adopted Method</u>	<u>Proposed Method</u>
Benzene	ASTM D3606-87 MLD 116 (If ethanol present)	ASTM D5580-9x
Aromatic Hydrocarbons	MLD 116	ASTM D5580-9x
Olefins	ASTM D1319-89	ASTM D1319-9x ^a
Sulfur ^b 30 ppm and above	ASTM D2622-87	ASTM D2622-94 ^{a,c} or ASTM D5453-93 with correlation to ASTM D2622-94
1 ppm to < 30ppm		ASTM D5453-93

^a The precision statements for these methods are defined in Attachments A and B and not by those published with the methods!

^b Separate test methods are proposed for the measurement of sulfur in different concentration ranges.

^c Revised calibration procedures for low level sulfur are shown in Attachment C.

II. BACKGROUND

A. California Regulations

In late 1991, the Board adopted the Phase 2 reformulated gasoline (Phase 2 RFG) regulations, which establish specifications for eight properties of California gasoline starting in March 1996. These include year-round minimum and maximum oxygen content limits, limits on the total benzene, aromatic hydrocarbon, olefin, and sulfur content, and limits on the volatility (RVP) and boiling point distribution (T50/T90) of gasoline. The Phase 2 RFG specifications are shown below in Table 2.

Table 2. Phase 2 Reformulated Gasoline Specifications

<u>Parameter</u>	<u>Flat Limit</u>	<u>Averaging Limit</u>	<u>Cap Limit</u>
Sulfur, ppm	40	30	80
Benzene, vol %	1.00	0.80	1.20
Olefins, vol %	6.0	4.0	10.0
Oxygen, wt %	1.8-2.2	--	2.7(max) 1.8(min) ^a
T90, °F	300	290 ^b	330
T50, °F	210	200	220
Aromatics, vol %	25	22	30
RVP, psi ^c	7.0	--	7.0

^aApplies in wintertime only

^b310°F cap applies to those refiners which average their fuel blends

^cSummertime only

B. Test Method Development

The Phase 2 RFG regulations designated the test methods to be used in measuring the fuel components. As directed by the Board when the regulations were adopted, we have been actively involved in identifying, developing, and refining test methods to measure benzene, aromatic hydrocarbons, olefins, and sulfur. ARB staff, working with WSPA, formed the CARB/WSPA Working Group on Fuels Test Methods and met biannually to discuss progress in methods development.

We also took an active role in the activities of ASTM Subcommittee D2 on Hydrocarbon Analysis, participating in many of their interlaboratory (round robin) studies of candidate methods. During this period, we also reviewed and approved a number of industry-proposed alternative methods as equivalent methods.

In evaluating test methods for adoption, a primary consideration is the precision of the test method. One measure of precision, reproducibility, is particularly applicable to interlaboratory comparisons. The ASTM uses the following language to define 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 [in the reproducibility table] in one case in twenty.

In addition to precision, we also considered factors such as cost, practicality, reliability, and the underlying technology. We gave greater weight to methods based on proven technology.

The ARB often identifies ASTM test methods as the means to determine compliance with its standards for motor vehicle fuels. The ASTM is a prominent not-for-profit organization that provides a forum for manufacturers and users of products, as well as academicians and government representatives, to prepare standards based on a consensus approach. Test methods are among the standards adopted by the ASTM. ASTM test methods are given an identification number with the year of approval indicated by the last two numbers following the hyphen, e.g., ASTM D3606-87 was approved in 1987. Draft test methods, i.e., those that have not yet been approved through ASTM's formal balloting process, are indicated by the notation "-9x."

C. Equivalent Methods

ARB regulations permit the use of test methods other than those adopted by rulemaking, if it is shown that they produce results that are equivalent to the adopted method. (13 CCR section 2263(c).) In determining if a candidate method is equivalent, ARB staff review the level of agreement in results between the candidate and adopted method as well as the precision of the candidate method relative to the adopted method.

D. Federal Regulations

The U.S. Environmental Protection Agency (U.S. EPA) administers regulations requiring that gasoline sold in areas with poor air quality meet standards for "federal" reformulated gasoline. These regulations have been applied in most of Southern California since December 1994. The test methods required by U.S. EPA are summarized in Table 3.

Table 3. Required EPA Methodologies

<u>Specifications</u>	<u>Test Method</u>
Benzene	ASTM D3606-92
Aromatic Hydrocarbons	GC/MS
Olefins	ASTM D1319-93
Sulfur	ASTM D2622-92

The federal regulations provide that aromatic hydrocarbon content is to be determined by a gas chromatographic procedure using a mass selective detector (GC/MS). Until January 1, 1997, refiners and importers are allowed to use ASTM D1319-93 as long as the results are correlated with U.S. EPA's GC/MS method. (40 C.F.R. sec. 80.46(f)(3).) The federal regulations allow producers and importers of California gasoline to use a test method specified in the ARB's Phase 2 RFG regulations in lieu of the otherwise applicable federal method. (40 C.F.R. sec. 80.81(h).)

III. RECOMMENDATION

We recommend that the Board amend section 2263(b), title 13, California Code of Regulations as indicated in Table 1. The amendments would update the methods designated for determining the benzene, aromatic hydrocarbon, olefin, and sulfur content of Phase 2 RFG. The text of the proposed amendments is set forth in Attachment D.

IV. PROPOSED ACTIONS, RATIONALE AND ALTERNATIVES

In this section, we evaluate the proposed test methods, the currently adopted test methods, and alternative test methods for measuring benzene, aromatic hydrocarbons, olefins, and sulfur in gasoline.

A. Replace ASTM D3606-87 and MLD 116 with ASTM D5580-9x for the Measurement of Benzene in Gasoline.

ASTM Method D3606-87 is the method currently required for the measurement of benzene in gasoline, and MLD 116 is the method required for the measurement of benzene in gasohol--gasolines containing ethanol. We recommend that the Board adopt ASTM D5580-9x to replace the current methods.

ASTM D5580-9x is proposed because it has better reproducibility (see Table 4) than the currently adopted method, ASTM D3606-87, and provides an opportunity for cost savings because it can also be used for measuring total aromatic hydrocarbons under the RFG 2 regulations.

1. Comparison of Adopted and Proposed Method

The proposed method, ASTM D5580-9x, uses gas chromatography techniques to achieve the separation and quantitation of benzene. This method completely separates oxygenates and other non-aromatic hydrocarbons from aromatic hydrocarbons and, therefore, can be used to measure benzene in gasolines containing ethanol and other oxygenates.

ASTM D5580-9x utilizes hardware that is only slightly more expensive than ASTM D3606-87. However, the additional cost is offset by the ability

1. The proposed regulations incorporate by reference various ASTM test methods. Published test methods are available directly from ASTM. You can obtain a copy of any published test method by writing to ASTM at 1916 Race Street, Philadelphia, Pennsylvania 19103, or by telephone at (215) 299-5585 or facsimile at (215) 977-9679 until September 30, 1995. Beginning October 1, 1995 ASTM can be reached at 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428-2959, (610) 832-9585, or FAX (610) 832-9555. Draft ASTM test methods can be obtained from the ARB contact person identified in the Notice of Proposed Rulemaking for the purpose of commenting on the proposed rulemaking.

to consolidate the analyses for two regulated components (benzene, total aromatic hydrocarbons) on one instrument.

ASTM D3606-87 was developed prior to the widespread use of oxygenated gasolines and does not separate benzene from methanol and ethanol. For this reason, MLD 116, which does not have the ethanol interference, was adopted for gasolines containing ethanol. However, tests on reformulated gasoline which became available after that rulemaking showed that benzene measurements using MLD 116 have a slight high bias indicating a possible interference.

The reproducibility of each method for the measurement of benzene is shown in Table 4. The proposed test method, ASTM D5580-9x, is more reproducible than ASTM D3606-87, the currently adopted version of ASTM D3606 or ASTM D3606-9x, the latest draft revision of the same method.

The proposed method was included in an ASTM-sponsored interlaboratory study comparing methods for measuring benzene and aromatic hydrocarbons in gasoline. Included in the study were laboratories using ASTM D3606-9x (revised version of the currently adopted method), ASTM D5580, GC/FTIR (draft ASTM), GC/MS (draft ASTM) and ASTM D1319 (for aromatics only). Because all of the methods were run on the same set of samples, an evaluation of bias among the methods was made. It was found that there was no significant bias among all of the methods for measuring benzene in gasoline.

Table 4. Reproducibility Comparison at 1.0 Vol% Benzene

<u>Test Method</u>	<u>Reproducibility</u>
D3606-87	0.28
D3606-9x	0.18
D5580-9x	0.14
GC/MS	0.11
GC/FTIR	0.09

2. Alternative Methods

a. Gas Chromatograph/Fourier Transform Infra Red (GC/FTIR)

Although GC/FTIR has a number of advantages, we do not recommend it for adoption because the instrument required for this method is relatively costly and continued vendor support for the instrument and software is questionable.

GC/FTIR is a draft ASTM method originally developed by Mobil Research and Development Company for measuring oxygenates in gasoline and subsequently expanded to include the analysis of benzene and aromatic hydrocarbons in gasoline. GC/FTIR is very selective for benzene because it uses the unique infra-red absorbance that is characteristic only of benzene.

Interlaboratory testing has shown the method to be very reproducible (see Table 4).

However, the GC/FTIR method has not received general industry support because of its greater cost and complexity of operation. A GC/FTIR instrument costs approximately twice as much as the GC/FID instrument used to carry out ASTM D5580. Furthermore, a major vendor has discontinued sales of the GC/FTIR instrument.

b. Gas Chromatography/Mass Spectrometry (GC/MS)

We do not recommend adoption of the GC/MS method as the designated test method for benzene due to its higher cost and the problems associated with the aromatic hydrocarbon determination which is linked to the same test method.

Gas chromatography coupled with mass spectrometry (GC/MS) is another selective technique for identifying and quantifying organic compounds. ASTM participants recently tested a draft GC/MS method for measuring benzene and other aromatic compounds. The method is discussed in more detail in section B.2.a.

The GC/MS instrument is more expensive than the GC/FID used to carry out the proposed method (ASTM D5580). Furthermore, because of concerns about the accuracy of the method for measuring aromatic hydrocarbons (see discussion below), the GC/MS method as presently written could only be used for the determination of benzene. Industry laboratories seeking to implement ARB adopted test methods would have to set up separate test methods for measuring benzene and aromatic hydrocarbons. This would further add to the cost and complexity of carrying out these analyses.

B. Replace MLD 116 with ASTM D5580-9x for the Measurement of Aromatic Hydrocarbons in Gasoline.

1. Comparison of Proposed and Adopted Methods

We recommend replacing MLD 116 with ASTM D5580 for measuring the aromatic hydrocarbon content of Phase 2 gasoline because the proposed method has several advantages over the current method. As indicated above, MLD 116 cannot be used for this purpose due to potential interferences. Furthermore, higher alcohols such as n-butanol and 2-butanol may also interfere with the aromatic hydrocarbons determination. ASTM D5580 has no known interferences in Phase 2 gasoline.

The currently adopted method, MLD 116, uses capillary gas chromatography with a selective detector, the photoionization detector (PID), to quantify benzene, and a FID to quantify the higher aromatic compounds.

The proposed method, ASTM D5580-9x, is based on gas chromatography with conventional flame ionization detection. Two columns and valves for reversing carrier gas flow (backflushing) are used to achieve complete

separation of the aromatic fraction from oxygenates and other classes of hydrocarbons. Total aromatic hydrocarbon concentration is obtained by carrying out two successive runs with different backflush times. In the first run, benzene and toluene are quantified. In the second run, aromatics with a carbon number of eight, such as ethylbenzene, p/m-xylene, and o-xylene are quantified and aromatics with a carbon number of nine and heavier are quantified as an integrated sum. Total aromatic hydrocarbons are quantified by adding the aromatic hydrocarbons determined in the first run to the aromatic hydrocarbons determined in the second run.

The instrumentation for this method is very similar to that required for measuring oxygenates in gasoline by ASTM D4815-94; therefore, both analyses could be carried out using one instrument.

2. Alternative Methods

In addition to proposed method ASTM D5580-9x, a number of alternative methods were reviewed for possible adoption as the designated test method for measuring aromatic hydrocarbons in gasoline. ASTM D5580-9x is the most reproducible of all of the evaluated methods (see Table 5).

Table 5. Reproducibility Comparison at 25 Vol% Total Aromatics

<u>Test Method</u>	<u>Reproducibility</u>
D5580-9x	1.4
GC/MS	3.1
GC/FTIR	1.6
D1319-9x	3.7

ASTM-sponsored interlaboratory testing for the methods shown in Table 5 also revealed differences in average results for the same sample set. ASTM D5580 shows higher results than other methods especially when results are expressed in volume percent. Further testing is underway at several laboratories to investigate the source(s) of the discrepancy among these aromatics test methods.

Other concerns we have with the alternative methods include cost, accuracy, and practicality. These are discussed in more detail below.

a. GC/MS

We do not recommend adoption of the GC/MS method for aromatic hydrocarbons because interlaboratory testing has revealed several technical problems. ASTM Subcommittee D2 is making substantial revisions to the method and will subject the revised method to further testing.

As discussed above, the U.S. EPA designated the GC/MS technique for measuring aromatic hydrocarbons in gasoline. However, the GC/MS technique as described in the Federal Register does not provide sufficient detail on

operating procedures to meet ASTM standards, and, therefore, ASTM participants prepared a draft GC/MS method for interlaboratory testing.

The GC/MS method speciates approximately sixty individual aromatic compounds in gasoline using the mass selective detector for quantitation. Because the mass selective detector does not respond uniformly to individual aromatic compounds, approximately twenty-five of the major aromatic compounds are calibrated individually. The response for the remaining, minor, aromatic compounds is based on several representative compounds. The calibration of 25 compounds at five concentration levels is relatively time consuming. Furthermore, the use of an assumed response factor can produce an inaccuracy in the method, especially if the fraction of aromatic compounds determined by an assumed response factor is large.

The GC/MS method has the advantage of being highly selective for aromatic compounds and, therefore, less prone to interferences. However, to date, round robin testing of the method has shown the GC/MS method to have poor reproducibility compared to ASTM D5580-9x and to be biased low compared to all other methods.

b. GC/FTIR

We do not recommend adoption of the GC/FTIR method for aromatic hydrocarbons because of its cost and because there is concern about continued vendor support for the method instrumentation and software. However, we recognize that this method has an advantage in that it can consolidate several analyses in one run (see A.2.a.), and it is similar in precision to our proposed method.

The GC/FTIR is similar to the GC/MS method in that it speciates approximately sixty aromatic compounds, calibrates with approximately twenty-five of the most significant aromatic compounds, and assumes a uniform response for the less significant compounds.

The GC/FTIR instrument is about twice as expensive as the GC/FID instrument needed for ASTM D5580. A major instrument vendor has discontinued sale of the GC/FTIR instrument and software.

c. ASTM D1319-9x

We do not recommend adoption of ASTM D1319-9x for measuring the aromatic hydrocarbon content of gasoline for several reasons. As shown in Table 5 (above), this test method is the least reproducible of the methods considered. In addition, although the equipment cost for ASTM D1319-9x is very small compared to the proposed method, it is relatively labor intensive, not readily automated, and not easily implemented in the field.

ASTM D1319-9x is based on elution chromatography. The gasoline sample is pumped down a highly polar silica gel column impregnated with indicator dyes. As the gasoline sample separates into individual fractions, the indicator dyes interact uniquely with each hydrocarbon type (aromatic, olefinic, paraffinic) to give a unique fluorescent color band which is

visible under ultraviolet light. The length of the colored band due to aromatic hydrocarbons compared to the length of the band of the total gasoline sample is the measure of volumetric concentration of the aromatic fraction.

- C. Replace ASTM D1319-89 with ASTM D1319-9x for the Measurement of Olefins in Gasoline. Adopt a revised precision statement for ASTM D1319-9x.

1. Comparison of Proposed and Adopted Methods

We recommend adoption of ASTM D1319-9x for measuring olefins in gasoline because it is more directly applicable to Phase 2 gasoline than the currently adopted method. Furthermore, we recommend adopting a revised precision statement because the current statement is outdated and is not applicable to oxygenated gasolines.

The ASTM D1319 test method is based on the principles of elution chromatography discussed above. The proposed method, ASTM D1319-9x, is identical to the current method, D1319-89, except that the scope is expanded to include oxygenated gasolines and the calculation of olefins is corrected for oxygenates. ASTM D1319-89 would provide erroneous results if not corrected for the oxygenate content of the gasoline.

The precision statement of the currently adopted method was based on interlaboratory testing carried out on non-oxygenated gasolines and is not applicable to oxygenated gasolines. Although ASTM D1319-9x adds language expanding the scope of the method to oxygenated gasolines, its precision statement does not address oxygenated gasolines. The proposed precision statement (see Attachment A) was derived from recent ASTM-sponsored interlaboratory testing using oxygenated gasolines and will eventually be added to the test method.

2. Alternative Methods

We have not identified any alternative methods for measuring olefins in gasoline at this time. However, we are monitoring the development of methods based on multidimensional gas chromatography developed by an independent contractor and a method based on supercritical fluid chromatography coupled with flame ionization detection.

- D. Make the following changes with respect to the adopted test method for measuring sulfur in gasoline:

- (1) Replace ASTM D2622-87 with ASTM D2622-94 for measuring sulfur in gasoline containing levels of 30 ppm and greater. Adopt a revised calibration procedure and precision statement for ASTM D2622-94 (see Attachments C and B).
- (2) Designate ASTM D5453-93 for measuring sulfur in gasoline at levels of 1 ppm to less than 30 ppm.

- (3) Allow the use of ASTM D5453-93 as an alternate method for measuring sulfur in gasoline at levels of 30 ppm and above when a correlation is established to ASTM D2622-94. Measurements made using ASTM D5453-93 must be corrected for any bias relative to ASTM D2622-94.

We recommend a number of changes to the designated test method for sulfur. The changes will significantly improve the precision of the test method both at the sulfur concentrations targeted by the RFG 2 regulations and the low sulfur levels we expect to see under the regulations, while providing the maximum level of flexibility in testing. In the following paragraphs, each of the proposed changes is discussed in greater detail.

1. Replace ASTM D2622-87 with D2622-94 and revise the calibration procedure and precision statement.

The proposed and adopted methods for sulfur are identical in terms of instrumentation, operating parameters, and published precision. ASTM D2622-94, however, contains several editorial changes which clarify the method.

The published precision of ASTM D2622-94 is based on an interlaboratory study carried out over thirteen years ago and, for the following reasons, may not be representative of the method's current precision for sulfur in gasoline:

- (a) It does not reflect the newer types of instruments.
- (b) The interlaboratory study was carried out on a mix of fuel types which included lubricating oils and diesel fuel but not Phase 2 gasoline.
- (c) The study was carried out with instruments calibrated on a wide range of sulfur concentrations.

Consequently, the reproducibility published with ASTM D2622-94 is very poor at the targeted levels of sulfur in Phase 2 gasoline (30-40 ppm).

To update the precision of ASTM D2622 and other methods for determining low level sulfur in gasoline, the WSPA/ARB Working Group on Fuels Test Methods recently completed interlaboratory testing. The results of this testing are shown in Table 6. We propose that a precision statement reflecting this data replace the precision statement published with the respective ASTM Method for determining low level sulfur concentration in gasoline.

Table 6. Reproducibility of ASTM D2622 from WSPA interlaboratory testing

<u>Sulfur Content, ppm</u>	<u>Reproducibility</u>
10 to 30	89.5% X Sulfur Content (ppm)
30 to 60	25.7% X Sulfur Content (ppm)
60 to 100	18.9% X Sulfur Content (ppm)

We also propose that the calibration procedure be modified to make the method more accurate for the measurement of sulfur in low-level sulfur gasoline. The modified procedure, set out in footnote c to the table designating the test methods in section 2263(b), title 13, CCR, is to supersede the calibration procedure as currently defined in ASTM D2622-94. The proposed change in calibration procedure is important also because it is similar to the procedure for the calibration of ASTM D5453-93, and thereby reduces the potential for bias between the methods.

Finally, we propose that results obtained from ASTM D2622-94 showing a sulfur concentration of 30 ppm or less be reported as 30 ppm. This is because the measurements become very imprecise below that concentration level.

2. Designate ASTM D5453-93 for the measurement of low-level sulfur.

ARB's Phase 2 RFG regulations allow the use of averaging for different batches of gasoline. This means that one blend of low sulfur gasoline can be used as an "offset" for a blend of higher sulfur gasoline. Phase 2 RFG regulations also allow alternative formulations when these are demonstrated, by the predictive model or emissions testing, to produce the same air quality benefits as the flat limits. Because of these regulatory allowances, it is very likely that many Phase 2 gasoline blends will have sulfur levels below the detection limit of ASTM D2622 and these sulfur levels will have to be verified for compliance purposes. Therefore, we propose the designation of ASTM D5453-93 for the measurement and reporting of sulfur concentrations below 30 ppm.

Unlike ASTM D2622 which utilizes X-Ray spectrometry, ASTM D5453-93 utilizes a pyrolysis technique in which the gasoline sulfur is converted to sulfur dioxide. The sulfur dioxide concentration is then determined from its ultraviolet fluorescence. Precision data published with the method indicate that the method is relatively reproducible in the concentration range of 1-30 ppm.

3. Use of ASTM D5453-93 above 30 ppm.

The reproducibility of ASTM D5453-93 at sulfur concentrations above 30 ppm is comparable to ASTM D2622-94. However, there is evidence that ASTM D5453-93 is biased low relative to ASTM D2622-94; therefore, we propose that both methods be permitted for analysis in this concentration region, but that each user of ASTM D5453-93 establish an equation correlating sulfur concentrations determined by ASTM D5453 to those obtained using ASTM D2622. This correlation curve is to be used for reporting corrected values of sulfur.

4. Alternative Methods Considered.

In addition to proposed methods ASTM D2622 and ASTM D5453, we evaluated several alternative methods for measuring the sulfur content of gasoline, including ASTM D4294-90, ASTM D4045-92, and ASTM D3120-92. Recent

WSPA-sponsored round robin testing of gasolines at 30 ppm and above showed ASTM D2622 and ASTM D5453 to have comparable reproducibility. These reproducibilities were significantly better than those published for any of the alternative methods.

a. ASTM D4045

We do not recommend adoption of ASTM D4045 as the designated test method for sulfur because recent interlaboratory testing has shown it to be less reproducible than ASTM D5453 at 30 ppm and above.

With this method sulfur containing compounds are converted to hydrogen sulfide in a reductive environment. The resulting hydrogen sulfide is then further reacted with moistened lead acetate which is coated onto a tape. The formation rate of lead sulfide is used to quantify the sulfur content of the sample. The scope of the test method includes the determination of sulfur from 0.02 ppm to 10 ppm. Higher concentrations of the sulfur can be determined if the sample is diluted.

b. ASTM D3120

We do not recommend designation of ASTM D3120 as the test method for sulfur because it is less reproducible than either D2622-94 (see Attachment B) or ASTM D5453.

With this method sulfur containing compounds are pyrolyzed to sulfur dioxide under an oxidative environment. The subsequent product is titrated with triiodine to determine the amount of sulfur dioxide with respect to the total amount of sulfur content in the sample. The published relative reproducibility is 38 percent.

c. ASTM D4294

We do not recommend adoption of ASTM D4294 because the scope of the method precludes measurements of low sulfur gasoline.

ASTM D4294 utilizes energy-dispersive X-ray fluorescence spectroscopy for the direct measurement of total sulfur content. The method is not applicable to Phase 2 gasoline because the lower limit of the method is 500 ppm whereas the Phase 2 RFG regulations limit sulfur to below 80 ppm (cap limit).

IV. AIR QUALITY, ENVIRONMENTAL AND ECONOMIC IMPACTS

A. Air Quality and Environmental Impacts

The proposed changes in the test methods will not result in air quality impacts because the underlying standards for gasoline content will remain the same. The staff has not identified any significant adverse non-air quality environmental impacts that would result from the proposal.

B. Economic Impacts

This section evaluates the potential economic impact of the proposed changes in the test methods on business enterprises in California. Government Code section 11346.3(a) requires that, in proposing to adopt or amend an administrative regulation, state agencies shall assess the potential for adverse economic impact on California business enterprises and individuals. The assessment shall also include the impact of the proposed or amended regulation on the ability of California businesses to compete with businesses in other states. In addition, Government Code section 11346.3(b) requires state agencies to assess the potential impact of their regulations on California jobs and business expansion, elimination, or creation.

The proposed changes in the test methods are intended to increase the precision and accuracy of the test methods currently used for measuring the benzene, aromatic hydrocarbon, olefin, and sulfur content of gasoline. These changes are not expected to impose significant additional costs on California business enterprises. The test methods update may actually result in cost savings to some affected businesses due to the combination of benzene and aromatics determinations in a single instrument. The table below summarizes the method changes, additional instrumentation cost, and difference in operational/maintenance (O/M) cost with comparison to those of existing regulatory requirements.

<u>Parameter</u>	<u>Current Method</u>	<u>Proposed Method</u>	<u>Instrument</u>	<u>O/M Cost</u>
Sulfur	D2622-87	D2622-94	none	none
		D5453-93	-\$37,000	-\$5,000
Olefins	D1319-89	D1319-9x	none	none
Benzene	D3606-87	D5580-9x	-\$10,000	similar
Aromatics	MLD 116	D5580-9x	-\$10,000	similar

The proposed method ASTM D2622-94 imposes no additional cost on affected businesses because it only requires minor editorial changes to the current method ASTM D2622-87. Refiners or fuel producers need to set up ASTM D5453 if they choose to comply with the Phase 2 RFG sulfur specification using options other than the flat limits.

The equipment cost for ASTM D5453 ranges from \$26,000 to \$47,000, depending upon the sophistication of the sample and data handling systems. Using the average cost of \$37,000 for the instrument and assuming 5 years useful life of the instrument, the annualized capital cost is estimated to be around \$9,000. Assuming annual O/M costs of \$5,000, total annualized costs of the instrument will be around \$14,000. The proposed change in the test method may require training of staff. The training cost is approximately \$1,200. No additional staff is expected to be needed since ASTM D5453 is fairly simple to carry out.

For olefin analysis, ASTM D1319-9x extends the scope of the adopted method to include the oxygenate containing blends. The test method requires a correction for the oxygenate contribution and reports the olefin concentration on a total sample basis. The test method specified for determining oxygenate content, ASTM D4815-94, is also ARB's designated test procedure for measuring oxygen content in California gasoline. Because all California gasoline requires no less than 1.8 and no greater than 2.2 percent oxygen by weight and the content of the oxygenates should be determined, the test method update to ASTM D1319-9x would not result in any cost increase.

For the benzene and aromatic hydrocarbon determinations, it will cost about \$10,000 in additional equipment for each GC modification. The current test methods, D3606 and MLD 116, and the proposed test method, D5580, all use GCs and similar detectors, thus the cost of O/M is not expected to increase. Because of the similarity in the equipment used for ASTM D5580 and ASTM D4815 (the test method specified for measuring the oxygen content of gasoline), the training cost for the analyst should be minimal. The proposed test methods for benzene and aromatic hydrocarbons may even result in cost savings because they require one analysis to measure both components.

Refiners or fuel producers typically need only one or no more than two of each instrument to comply with the regulations. The proposed test methods are projected to cost the affected industry less than \$2,000,000 in total. This cost increase is not expected to have a significant impact on the profitability of California refiners or fuel producers. As a result, we expect no significant change in employment, business competitiveness, and the status of businesses in California due to the change of test methods. However, to the extent that refiners or fuel producers purchase new instruments from California businesses, some jobs may be created in businesses manufacturing, distributing, and selling those instruments.

REFERENCES

1. ASTM D 1319-9x, "Proposed Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption." Draft ASTM test method under the jurisdiction of Committee D.02 on Petroleum Products and Lubricants.
2. ASTM D 770, "Specification for Isopropyl Alcohol," Annual Book of ASTM Standards, Vol 06.04.
3. ASTM D 2001, "Test Method for Depentanization of Gasoline and Naphthas," Annual Book of ASTM Standards, Vol 05.01.
4. ASTM D 2427, "Test Method for Determination of C₂ through C₅ Hydrocarbons in Gasolines by Gas Chromatography," Annual Book of ASTM Standards, Vol 05.01.
5. ASTM D 2710, "Test Method for Bromine Index of Petroleum Hydrocarbons by Electrometric Titration," Annual Book of ASTM Standards, Vol 05.02.
6. ASTM D 3663, "Test Method for Surface Area of Catalysts," Annual Book of ASTM Standards, Vol 05.03.
7. ASTM D 4057, "Practice for Manual Sampling of Petroleum and Petroleum Products," Annual Book of ASTM Standards, Vol 05.02.
8. ASTM D 4815, "Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C₁ to C₄ Alcohols in Gasoline by Gas Chromatography," Annual Book of ASTM Standards, Vol 05.03.
9. ASTM E 11, "Specification for Wire-Cloth Sieves for Testing Purposes," Annual Book of ASTM Standards, Vol 14.02.
10. ASTM D 5580-9x, "Proposed Standard Test Method for Determination of Benzene, Toluene, Ethylbenzene, p/m-Xylene, o-Xylene, C₉ and Heavier Aromatics and Total Aromatics in Finished Gasoline by Gas Chromatography," Draft ASTM method under the jurisdiction of Committee D.02 on Petroleum Products and Lubricants.
11. ASTM D 1298, "Practice for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method," Annual Book of ASTM Standards, Vol 05.01.
12. ASTM D 4052, "Test Method for Density and Relative Density of Liquids by Digital Density Meter," Annual Book of ASTM Standards, Vol 05.02.
13. ASTM D 4307, "Practice for Preparation of Liquid Blends for use as Analytical Standards," Annual Book of ASTM Standards, Vol 05.02.

14. ASTM E 355, "Practice for Gas Chromatography Terms and Relationships," Annual Book of ASTM Standards, Vol 14.01.
15. ASTM D 2622-94, "Standard Test Method for Sulfur in Petroleum Products by X-Ray Spectrometry," Annual Book of ASTM Standards, Vol 06.02.
16. ASTM D 5453-93, "Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels and Oils by Ultraviolet Fluorescence," Annual Book of ASTM Standards, Vol 05.03.
17. ASTM D 4177, "Practice for Automatic Sampling of Petroleum and Petroleum Products," Annual Book of ASTM Standards, Vol 05.02.

ATTACHMENT A

Modified Reproducibility of ASTM D1319-9x

Repeatability and Reproducibility - Oxygenate-Containing Samples^a

	<u>Range(vol%)</u>	<u>Repeatability</u>	<u>Reproducibility</u>
Aromatics	13 - 40	1.3	3.7
Olefins	4 - 33	0.258 (X) ^{0.6}	0.819 (X) ^{0.6}
Saturates	45 - 68	1.5	4.2

X = Volume %

^a The repeatability and reproducibility is based on draft test method "Proposed Revision of ASTM D1319-9x" Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption.

ATTACHMENT B

Proposed Reproducibility of ASTM D2622

Reproducibility of ASTM D2622 from WSPA interlaboratory testing

<u>Sulfur Content, ppm</u>	<u>Reproducibility, ppm</u>
10 to 30	89.5% X Sulfur Content (ppm)
30 to 60	25.7% X Sulfur Content (ppm)
60 to 100	18.9% X Sulfur Content (ppm)

ATTACHMENT C

ASTM D2622 Low Level Sulfur Calibration Procedure

Reagents

Thiophene, at least 99 % purity
2-Methylthiophene, at least 98 % purity
Toluene, reagent grade
2,2,4-Trimethylpentane, reagent grade

Preparation of Stock Standard

Weigh standard materials thiophene (~0.7290 gm) and 2-methylthiophene (~0.7031 gm) separately into a tared volumetric flask and record the individual mass to 0.1 mg. Add "mixed solvent" containing 25 % toluene and 75 % iso-octane (by volume) into the flask to a net weight of approximately 50 gm, and record the weight. This "Stock Standard" contains approximately 10 mg/gm sulfur. The actual sulfur concentration can be calculated as follows:

Sulfur from thiophene (gm) =
Weight of thiophene * 32.06 * purity / 84.14

Sulfur from 2-methylthiophene (gm) =
Weight of 2-methylthiophene * 32.06 * purity / 98.17

Sulfur concentration of Stock Standard (gm/gm) =
(sulfur from thiophene + sulfur from 2-methylthiophene) / net weight of
the stock standard

Multiply the sulfur concentration by 1000 to convert the units to mg/gm.

Preparation of Calibration Standards

Pipet 2.5 ml of the Stock Standard into a 250 ml flask and dilute with the "mixed solvent" to the mark. This "Diluted Standard" contains approximately 100 mg/kg sulfur. Prepare 1, 5, 10, 20, 30, 40, 50 ppm calibration standards by pipetting 1, 5, 10, 20, 30, 40, 50 ml of the Diluted Standard into a 100 ml flask, respectively, and diluting with the "mixed solvent" to the mark. The actual concentration of the calibration standard should be determined from the stock standard. The standards with the concentration ranging from 1 to 100 ppm are to be used for calibrating the instrument.

ATTACHMENT D

Amend section 2263(b), Title 13, California Code of Regulations, to read as follows:

Subarticle 2. Standards for Gasoline Sold Beginning March 1, 1996

* * * * *

Section 2263. Sampling Procedures and Test Methods

(a) Sampling Procedures.

In determining compliance with the standards set forth in this subarticle 2, an applicable sampling methodology set forth in 13 C.C.R. section 2296 shall be used.

(b) Test Methods.

(1) In determining compliance with the standards set forth in this subarticle 2, the test methods presented in Table 1 shall be used. All identified test methods are incorporated herein by reference.

Table 1

<u>Section</u>	<u>Gasoline Specification</u>	<u>Test Method</u>
2262.1.	Reid Vapor Pressure	ASTM D 323-58 ^a or 13 C.C.R. Section 2297
2262.2.	Sulfur Content 1 ppm to <30 ppm	ASTM D 2622-87 ASTM D 2622-94 ^{b,c,d,e} ASTM D 5453-93 ^{e,f}
2262.3	Benzene Content	ASTM 3606-87D 5580-9x or ARB MLD 116 b/
2262.4.	Olefin Content	ASTM D 1319-89-9x ^g
2262.5	Oxygen Content	ASTM D 4815-94
2262.6.	T90 and T50	ASTM D 86-90
2262.7.	Aromatic Hydrocarbon Content	ARB MLD 116 b/ ASTM D 5580-9x

^a Delete paragraph 4(b) concerning sampling.

~~b/~~ Air Resources Board, Monitoring and Laboratory Division, "Procedure for the Analysis of Benzene and Other Aromatic Components of Gasoline," dated November 1991. This method is to be used instead of ASTM 3606-87 to determine benzene content if ethanol is present.

^b Results showing sulfur concentration of 30 ppm or less using this method shall be reported as 30 ppm.

c. Make the following modifications to paragraph 9.1:

1. Low Level Sulfur Calibration Procedure

Reagents

Thiophene, at least 99 % purity

2-Methylthiophene, at least 98 % purity

Toluene, reagent grade

2,2,4-Trimethylpentane, reagent grade

Preparation of Stock Standard

Weigh standard materials thiophene (~0.7290 gm) and 2-methylthiophene (~0.7031 gm) separately into a tared volumetric flask and record the individual mass to 0.1 mg. Add "mixed solvent" containing 25 % toluene and 75 % iso-octane (by volume) into the flask to a net weight of approximately 50 gm, and record the weight. This "Stock Standard" contains approximately 10 mg/gm sulfur. The actual sulfur concentration can be calculated as follows:

Sulfur from thiophene (gm) =
Weight of thiophene * 32.06 * purity / 84.14

Sulfur from 2-methylthiophene (gm) =
Weight of 2-methylthiophene * 32.06 * purity / 98.17

Sulfur concentration of Stock Standard (gm/gm) =
(sulfur from thiophene + sulfur from 2-methylthiophene) / net weight of the stock standard

Multiply the sulfur concentration by 1000 to convert the unit to mg/gm.

Preparation of Calibration Standards

Pipet 2.5 ml of the Stock Standard to 250 ml flask and dilute with the "mixed solvent" to the mark. This "Diluted Standard" contains approximately 100 mg/kg sulfur. Prepare 1, 5, 10, 20, 30, 40, 50 ppm calibration standards by pipetting 1, 5, 10, 20, 30, 40, 50 ml of the Diluted Standard into a 100 ml flask, respectively, and diluting with the "mixed solvent" to the mark. The actual concentration of the calibration standard should be determined from the stock standard. The standards with the concentration ranging from 1 to 100 ppm are to be used for calibrating the instrument.

d. Replace ASTM D2622-94 reproducibility values with the following:

<u>Sulfur Content, ppm</u>	<u>Reproducibility</u>
<u>10 to 30</u>	<u>89.5% X Sulfur Content (ppm)</u>
<u>30 to 60</u>	<u>25.7% X Sulfur Content (ppm)</u>
<u>60 to 100</u>	<u>18.9% X Sulfur Content (ppm)</u>

e As an alternative to the designated test method (ASTM D2622-94), D5453-93 may be used for gasoline with sulfur concentrations of 30 ppm or above provided the results from testing with D5453-93 are correlated with ASTM D2622-94 as modified in c above.

f Report results as sulfur content no less than 1 ppm.

g Add reproducibility statements for oxygenate-containing samples

	<u>Range</u>	<u>Repeatability</u>	<u>Reproducibility</u>
<u>Aromatics</u>	<u>13 - 40</u>	<u>1.3</u>	<u>3.7</u>
<u>Olefins</u>	<u>4 - 33</u>	<u>0.258 (X) 0.6</u>	<u>0.819 (X) 0.6</u>
<u>Saturates</u>	<u>45 - 68</u>	<u>1.5</u>	<u>4.2</u>

X = Volume %

(c) Equivalent Methods.

Whenever this section provides for the use of a specified test method, another test method may be used following a determination by the executive officer that the other method produces results equivalent to the results with the specified method.

NOTE: Authority cited: Health and Safety Code Sections 39600, 39601, 43013, 43018 and 43101; and Western Oil and Gas Ass'n. v. Orange County Air Pollution Control District, 14 Cal.3d 411, 121 Cal.Rptr. 249 (1975).
Reference: Health and Safety Code Sections 39000, 39001, 39002, 39003, 39010, 39500, 39515, 39516, 39606, 41511, 43000, 43016, 43018, and 43101; and Western Oil and Gas Ass'n. v. Orange County Air Pollution Control District, 14 Cal.3d 411, 121 Cal.Rptr. 249 (1975).