STATE OF CALIFORNIA
CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY
AIR RESOURCES BOARD

STAFF REPORT: INITIAL STATEMENT OF REASONS FOR RULEMAKING

PUBLIC HEARING TO CONSIDER AMENDING THE TEST METHODS DESIGNATED FOR DETERMINING OLEFIN CONTENT AND DISTILLATION TEMPERATURES OF GASOLINE

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I. INTRODUCTION AND SUMMARY

The staff of the Air Resources Board (ARB or Board) is proposing that the ARB amend its designations of the test methods used to measure the amount of olefins in and the distillation temperatures of California Reformulated Gasoline (CaRFG). The updated test methods will be used to determine if motor vehicle gasolines comply with ARB's regulations.

The Board adopted the Phase 2 CaRFG regulations in November 1991, with an effective date of March 1, 1996. The Phase 2 specifications, now contained in section 2262, title 13, California Code of Regulations (CCR), include limits on olefins and on T50 and T90 – the temperatures at which 50 percent and 90 percent of the gasoline is distilled. The test methods for determining compliance with these limits are specified in section 2263(b), title 13, CCR.

In December 1999, the Board adopted standards for Phase 3 CaRFG, applicable starting December 31, 2002. The specifications for distillation temperatures were changed while the olefin specifications remained the same. The section 2263(b) test methods also apply to the Phase 3 CaRFG standards.

Although the originally specified test methods were the best procedures available when the CBG 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. Since 1995, this process has resulted in improvements to several of the test methods.

To further this end, over the last 5 years we have conducted in-house evaluations of various test methods, participated in interlaboratory studies of test method precision carried out by the American Society for Testing and Materials (ASTM), and met regularly with members of the Western States Petroleum Association (WSPA) to discuss test method development. We also held three 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 olefin content and distillation temperatures. The proposed test method for olefins using supercritical fluid chromatography (SFC) is two to three times more precise than the method currently designated by the ARB. The proposed distillation test method is an updated version of the currently designated method, which contains various correction and clarifications and eliminates certain unnecessary and burdensome requirements. The proposed changes are set out in Table 1.

Table 1. Proposed Test Method Changes

Regulated Component	Currently Adopted Method	Proposed Method
Olefins	ASTM D1319-95a	ASTM D6550-00[a] (SFC)
Distillation Temperatures	ASTM D86-90	ASTM D86-99aε1

a. The precision statement for this method (by SFC) is defined in Attachment A and not by the statement published with the method. Mass-volume% correlation procedures are shown in Attachment B. A revised scope statement is given in Attachment C.

PLAIN ENGLISH SUMMARY

The new test method staff is proposing uses a complex, automatic system controlled by a computer to count the olefins in a sample of gasoline. The current method counts olefins by having a human operator measure the length of a glowing band with a ruler. With the new method, two people measuring the same gasoline sample are much more likely to get the same answer than they are with the old method.

II. BACKGROUND

A. California Regulations

In late 1991, the Board adopted the Phase 2 CaRFG 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 CaRFG specifications are shown below in Table 2.

Table 2. Phase 2 CaRFG Specifications

Parameter	Flat Limit	Averaging Limit	Cap Limit
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	--	1.8[a] – 3.5
T50, ^{o}F	210	200	220
T90, ^{o}F	300	290	330
RVP, psi[b]	7.0	--	7.0

a - Minimum applies in wintertime only
b - RVP limit applies in summertime only

The CaRFG regulations identify the test methods to be used in determining compliance with the limits for the eight regulated properties. In almost all cases, they are ASTM test methods, sometimes with specified modifications. 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. The last two digits of an ASTM Test Method designation represent the year of adoption or last revision.

B. Test Method Development

1. Olefin Analysis

The original Phase 2 CaRFG regulations specified ASTM D1319-89, fluorescent indicator adsorption (FIA), for the measurement of olefins. The regulation was amended in October 1995, changing the designated test method to ASTM D1319-9x (later published and updated as D1319-95a). The newer version of the test method

includes precision data applicable to oxygenated gasolines, but is otherwise identical to the older version in most respects.

Although ASTM D1319 was the best method available when the regulations were adopted and amended, both ARB staff and industry recognized that it has a serious shortcoming. The test method has a very poor precision as measured by interlaboratory reproducibility. In adopting the regulations, the Board accordingly directed staff to work with industry to identify improved test procedures.

ARB staff, working with WSPA, formed the CARB/WSPA Working Group on Fuels Test Methods, which has met biannually to discuss progress in methods development. Staff has also taken an active role in the activities of ASTM Subcommittee D02.04 on Hydrocarbon Analysis, participating in many of their interlaboratory round robin studies of candidate methods.

Through its work with ASTM and WSPA, staff has identified three possible test methods to replace ASTM D1319-95a. Of these three methods, staff recommends a modified version of ASTM D6550-00, "Standard Test Method for the Determination of the Olefin Content of Gasolines by Supercritical Fluid Chromatography."

2. Distillation

The current CaRFG regulation specifies ASTM D86-90 as the designated test method for the measurement of distillation temperatures. After its adoption, errors were discovered in the precision statements of this method. A later version of the method, D86-96, contains corrected precision statements. As a result, method D86-96 was granted equivalency by Executive Order # G-719-003 in August, 1996.

The most recently published version of the distillation method, D86-99aε1, contains several important changes. The method now requires a temperature sensor centering device which improves the accuracy of the temperature reading. The specifications for the glassware used during the distillation have been corrected, ensuring the availability of appropriate equipment.

Two aspects of D86-90 which are difficult to implement are the time from first drop to 5% recovered (60-75 seconds) and the time from final heat adjustment to final boiling point (3-5 minutes). As a result of years of study and discussion, these requirements have been relaxed to 60-100 seconds and 0-5 minutes, respectively, in D86-99aε1.

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 olefin content and distillation temperatures of CaRFG. The text of the proposed amendments is set forth in Attachment D.

IV. PROPOSED ACTIONS, RATIONALE, AND ALTERNATIVES

In this section, the proposed test methods, the currently applicable test methods, and alternative test methods are evaluated.

A. Replace ASTM D1319-95a with ASTM D6550-00 (SFC) for the Measurement of Olefins in Gasoline, starting January 1, 2002. Adopt a mass-volume% correlation, revised precision statement, and expanded scope for ASTM D6550-00 (see Attachments A, B and C).

ASTM D1319-95a is the method currently designated for the measurement of olefins in gasoline. We recommend that the Board adopt ASTM D6550-00 to replace the current method.

The precision statement in the published version of ASTM D6550-00 is based on an interlaboratory round robin conducted by ASTM. After D6550-00 was balloted, certain participants in the round robin were found to have used impure calibration materials, resulting in a poor reproducibility for the method. CARB and WSPA performed an independent round robin in March 2000 in order to determine a more realistic precision statement. The precision statement derived from the CARB/WSPA round robin is given in Attachment A. The reproducibility of the proposed method is substantially better than the reproducibility of the currently applicable method.

WSPA members have expressed concern about the very low reproducibility determined from the CARB/WSPA round robin data. They believe that the reproducibility may be artificially low because most of the participating laboratories were research facilities and all the olefin trap columns were manufactured in a single batch. Staff will consider new precision data as it becomes available.

ASTM D6550-00 generates results in mass%, while the olefin regulation is in volume%. Measurements in these two units cannot be interconverted. A correlation equation was developed to convert mass% to volume% using data from D1319-95a. The equation is given in Attachment B. Since the correlation equation was developed using mostly Phase 2 gasolines, it may not give optimal results for future Phase 3 fuels. As Phase 3 CBG enters the marketplace, staff and WSPA will monitor the accuracy of the correlation equation and propose a new equation if necessary.

ASTM D6550-00's published range is 1 to 25 mass% olefins. No samples with olefin levels below 1 mass% were used in either the ASTM or CARB/WSPA round robin. However, certain refiners in California routinely produce gasoline with olefin levels well below 1 mass%. Staff and WSPA scientists agree that there is no inherent reason that D6550-00 should not perform acceptably at lower olefin levels. An expanded scope statement is given in Attachment C. In the future, staff and WSPA will verify the ability of D6550-00 to measure these lower olefin levels.

Implementation of D6550-00 will require the purchase and setup of new instruments or modification of existing instruments. Additionally, refinery staff will need training and practice in conducting the new test method. In order to ensure that refiners have sufficient time to develop expertise in the new method, staff recommends a start date of January 1, 2002.

The three technical, quantitative amendments to ASTM D6550-00 described above may require adjustment as new data are obtained. Staff recognizes the possibility that a more appropriate precision statement, correlation equation, and/or lower range limit may become available before the January 1, 2002 implementation date. Any changes to these equations and values would require a supplemental rulemaking. In order to facilitate any such changes, we recommend that the Board delegate authority to make these amendments to the Executive Officer.

1. Comparison of Adopted and Proposed Methods

   The proposed method, ASTM D6550-00, uses supercritical fluid chromatography (SFC) to achieve the separation and quantification of olefins. This method completely separates the olefinic fraction of the fuel from the saturate, aromatic, and oxygenate fractions. The olefins are quantified by electronic detection and computer integration. In contrast, ASTM D1319-95a measures olefins by elution of the gasoline onto a silica column impregnated with fluorescent dyes. Olefins are quantified by operator measurement of the lengths of different fluorescent bands using a ruler.

   ASTM D6550-00 utilizes hardware that is more expensive than ASTM D1319-9x. However, all refiners of California gasoline already use SFC instrumentation for compliance with the regulation of aromatics in diesel fuel. The cost of modifying the existing SFC units to measure olefins in gasoline as well as aromatics in diesel fuel is approximately

$10,000 per instrument. The additional cost may be offset by reduced labor costs associated with the SFC method.

ASTM D6550-00 generates results in mass%. These values are converted to vol% using a correlation equation (see Attachment B).

The reproducibility of each test method (including alternatives) is shown in Table 3. Values are given for olefin levels corresponding to the average, flat, and cap limits.

Table 3. Reproducibility Comparison at 4.0, 6.0, and 10.0 Vol% Olefins

Test Method	Reproducibility (R)	R @ 4.0 Vol%	R @ 6.0 Vol%	R @ 10.0 Vol%
D6550-00	$0.32X^{0.5}$	0.6	0.8	1.0
D1319-9x	$0.819X^{0.6}$	1.9	2.4	3.3
D6293-98	$0.255X^{0.7444}$	0.7	0.9	1.4
D6296-98	$0.26X^{0.72}$	0.7	0.9	1.4

2. Alternative Methods

a. ASTM D6293-98: Multidimensional Gas Chromatography (O-PONA)

Although ASTM D6293-98 has a number of advantages, we do not recommend it for adoption because the analysis requires nearly two hours per sample and the instrument is relatively costly and complex. The method's reproducibility is comparable to that of D6550-00, being slightly better for olefin concentrations below 3 vol% and slightly worse at higher concentrations. While D6293-98 has the advantage of providing results in volume%, the length of the analysis makes it undesirable for a production environment. Additionally, the instrumentation specified by D6293-98 is currently available from only one vendor.

ASTM D6293-98 is currently considered an equivalent method to D1319-9x, and it will be eligible for equivalency to ASTM D6550-00 once the latter is adopted.

b. ASTM D6296-98: Multidimensional Gas Chromatography (Fast Total Olefins)

ASTM D6296-98 is based on technology similar to that of D6293-98. This test method requires only 20 minutes per sample. However, it requires sample preparation and

calibration, and does not give as accurate a volume% result as D6293-98. It also has a high bias of about 10% compared to D6293-98. The instrument is also currently available from only one vendor.

B. Replace ASTM D86-90 with ASTM D86-99aε1.

ASTM D86-90 is the method currently designated for the measurement of T50 and T90 for gasoline. We recommend that the Board adopt the most recent published version, ASTM D86-99aε1, to replace the current method. Since the same basic hardware is used, and no additional training of personnel is required, there is no need to provide lead time for this amendment.

ASTM D86-90 contains errors in its precision statements. These errors have been corrected in D86-99aε1.

ASTM D86-99aε1 relaxes D86-90's overly restrictive requirements for the time from first drop to 5% recovered and the time from final heat adjustment to end point. Through extensive studies, ASTM's subcommittee on distillation found that relaxing these time requirements would not cause any loss of data quality. These changes will result in fewer repeat analyses being performed.

ASTM D86-99aε1 also specifies a mechanism for ensuring that the temperature sensor is centered in the neck of the distillation flask. Centering the sensor is necessary to obtain accurate temperature readings.

1. Comparison of Adopted and Proposed Methods

With the exception of the centering device, ASTM D86-99aε1 uses the same hardware as ASTM D86-90. No additional skills or training are required of the operator. The new method should result in lower costs due to the reduced need for repeat analyses.

2. Alternative Methods

No alternative methods were considered.

V. 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 this 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 11346.5(a)(8) 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. The Government Code also requires state agencies to assess the potential impact of their regulations on California jobs and business expansion, elimination, or creation.

The proposed changes are intended to increase the precision, accuracy, and efficiency of the test methods used for measuring the olefin content and distillation temperatures of CBG. 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 lower number of repeated tests required by the new distillation method. The table below summarizes the test method changes, additional instrumentation cost, and differences in operational/maintenance (O/M) cost resulting from the changes.

Parameter	Current Method	Proposed Method	Instrument Cost	O/M Cost
T50/T90	D86-90	D86-99aε1	none	none
Olefins	D1319-95a	D6550-00	~$10,000 - $65,000	~$0 - $6500

The proposed method D86-99aε1 imposes no additional cost on affected businesses because it requires only minor editorial changes to the current method D86-90.

The cost for D6550-00 varies greatly depending on whether businesses choose to upgrade an existing instrument already in use or purchase a new instrument. The SFC instrumentation used for analyzing diesel fuel for

aromatic content can be upgraded to analyze gasoline for olefins for approximately $10,000. In this case, the additional maintenance cost is minimal. However, refiners may choose to purchase an additional instrument rather than analyze both gasoline and diesel fuel on a single instrument. In this case, the instrument cost is approximately $65,000. Maintenance costs are typically estimated as 10% of the instrument cost. The cost of consumable materials is expected to be similar to that of D1319-95a.

Training costs for D6550-00 are expected to be minimal as refiners already have expertise in SFC. No additional staff is expected to be needed since D6550-00 is more automated and less labor-intensive than D1319-95a.

The proposed test methods are projected to cost the affected industry no more than $1,200,000 in total over five years. This cost increase is not expected to have a significant impact on the profitability of California refiners. As a result, we expect no significant change in employment, business competitiveness, or the status of businesses in California due to the change of test methods.

References

1. ASTM D86-99aε1, “Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure,” Annual Book of ASTM Standards, Vol. 05.01.

2. ASTM D1319-95a, “Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption,” Annual Book of ASTM Standards, Vol. 05.01.

3. ASTM D6293-98, “Standard Test Method for Oxygenates and Paraffin, Olefin, Naphthene, Aromatic (O-PONA) Hydrocarbon Types in Low-Olefin Spark Ignition Engine Fuels by Gas Chromatography,” Annual Book of ASTM Standards, Vol. 05.04.

4. ASTM D6296-98, “Standard Test Method for Total Olefins in Spark-Ignition Engine Fuels by Multidimensional Gas Chromatography,” Annual Book of ASTM Standards, Vol. 05.04.

5. ASTM D6550-00, “Standard Test Method for Determination of Olefin Content of Gasolines by Supercritical Fluid Chromatography,” Annual Book of ASTM Standards, Vol. 05.04 (forthcoming).

6. WSPA Round Robin Composite Results, distributed July 17, 2000.

All of the above ASTM test methods are available from ASTM at www.astm.org.

ATTACHMENT A

Modified Precision of ASTM D6550-00

Repeatability = $0.13X^{0.5}$

Reproducibility = $0.32X^{0.5}$

X = mass% olefins

These precision equations are based on a round robin study performed by CARB and WSPA in March-June 2000. The raw data from this study is available upon request. This round robin was carried out because some participants in the original ASTM round robin are known to have used impure calibration materials, resulting in a poor precision. Staff agrees to consider future precision studies as they become available.

ATTACHMENT B

Equation for Converting Mass% Olefins to Volume% Olefins

Volume% = 0.857 * Mass%

This equation is based on data from a CARB/WSPA round robin study in March-June 2000. The data is available upon request. CARB and WSPA will monitor the continued accuracy of this correlation as Phase 3 CBG begins production.

ATTACHMENT C

Modified Scope Statement for ASTM D6550-00

The application range is from 0.3 to 25 mass% total olefins.

In both the CARB/WSPA and ASTM round robins, no samples with olefin levels below 1 mass% were included. As a result, the published scope for D6550-00 is 1 to 25 mass%. Staff and WSPA scientists agree that there is no reason the method shouldn't be able to quantify olefins as low as 0.3 mass%, the lower limit of the current designated and equivalent test methods.

The extension of the scope statement is necessary, as there are refiners in California which routinely produce gasoline with olefin levels well below 1 mass%. Staff and WSPA have agreed to confirm the applicability of D6550-00 to low olefin levels in the near future.

ATTACHMENT D

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

[Note: The proposed amendments for this rulemaking action are shown in ~~strikethrough~~ to indicate proposed deletions and underline to indicate proposed additions.]

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

Section	***Gasoline Specification***	***Test Method*** [a]
2262.1	Reid Vapor Pressure	ASTM D 323-58 [b] or 13 C.C.R. Section 2297
2262.2	Sulfur Content	ASTM D 2622-94 [c, d] or ASTM D 5453-93
2262.3	Benzene Content	ASTM D 5580-95 [e]
2262.4	Olefin Content	~~ASTM D 1319-9X [f]~~ ASTM D 6550-00[f,g,h]
2262.5	Oxygen Content	ASTM D 4815-94
2262.6	T90 and T50	ASTM D 86-~~90~~-99aε1
2262.7	Aromatic Hydrocarbon Content	ASTM D 5580-95 ~~[g]~~ [i]

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a Do not report values below the limit of detection (LOD) specified in the test method. Where a test method does not specify a LOD, do not report values below the lower limit of the scope of the test method.

b Delete paragraph 4(b) concerning sampling.

c Make the following modifications to paragraph 9.1:

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 a mixed solvent containing 25% toluene and 75% isooctane (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
Pipette 2.5 ml of the Stock Standard to 250 ml flask and dilute with the mixed solvent to the mark. The diluted standard contains approximately 100 mg/kg sulfur. Prepare 5, 10, 20, 30, 50, 75 ppm calibration standards by pipetting 5, 10, 20, 30, 50, 75 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 concentration ranging from 5 to 100 ppm and the mixed solvent are to be used for calibrating the instrument.

d Replace ASTM D 2622-94 reproducibility values with the following:

Sulfur Content, ppm

10 to 30
>30

Reproducibility

40.5% X Sulfur Content (ppm)
19.2% X Sulfur Content (ppm)

e The reproducibility of benzene is as follows:

Reproducibility = 0.1409 ($X^{1.133}$), where X = vol %

~~f Add the following reproducibility statement for oxygenate-containing samples:~~

~~Olefins~~

~~Range~~

~~0.3 - 33~~

~~Reproducibility~~

~~0.819 (X) $^{0.6}$~~

~~X = Volume %~~

f Replace ASTM D6550-00 reproducibility equation with the following:

Reproducibility = 0.32 $X^{0.5}$
where X is between 0.3 and 25 mass % olefin

~~g The reproducibility of total aromatic hydrocarbon is as follows:~~

~~Reproducibility = 1.4 vol%~~

g The conversion from mass% olefin to volume% olefin is defined as follows:

volume% olefin = 0.857 * mass% olefin

h Replace the last sentence in ASTM D6550-00 section 1.1 with the following:

The application range is from 0.3 to 25 mass% total olefins.

i The reproducibility of total aromatic hydrocarbon is as follows:

Reproducibility = 1.4 vol%

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