# Appendix F

# Protocol and Protocol Amendments

**American Petroleum Institute**
1220 L Street, Northwest
Washington, D.C. 20005
(202) 682-8240

G. William Frick
Vice President
Health, Environment and Safety

April 8, 1996

John C. Sebastian
Chevron Reserach and Technology Company
100 Chevron Way
Richmond, CA 94802

Dear Mr. Sebastian:

The Agreement of December 29, 1995, between the American Petroleum Institute (API) and Chevron Research and Technology Company, Analytical Sciences Unit, Toxicology and Health Risk Assessment (Chevron), for a study entitled: "**Fuel Blending, Headspace Analysis, and Benchtop Vapor Generation for an Alternative Evaporative Emissions Generation Procedure Under Clean Air Act Section 211(b)**," is hereby modified as follows:

1. Chevron shall perform a change in methodology as described in the attached letter and revised cost estimates dated March 18, 1996 copies of which are attached hereto and made a part hereof.

2. Chevron shall perform all its obligations for an additional amount of nine thousand seven hundred forty dollars ($9,740). The Agreement amount not to be exceeded is increased by nine thousand seven hundred forty dollars ($9,740) from thirty-one thousand four hundred eighty-five dollars ($31,485) to forty-one thousand two hundred twenty-five dollars ($41,225).

In all other respects, the terms and conditions of the December 29, 1995, Agreement, as amended, shall remain in full force and effect.

If the foregoing is acceptable, please sign below and return one copy of this amendment to API.

CHEVRON RESEARCH AND TECHNOLOGY COMPANY

BY: John Sebastian
John C. Sebastian

DATE: April 15, 1996

AMERICAN PETROLEUM INSTITUTE

BY: G W Frick
G. W. Frick
Vice President, Health, Environment and Safety

BY: Del Persinger
Del Persinger
Assistant Secretary

DATE: April 8, 1996

An equal opportunity employer

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| | |
|---|---|
| To Bob Barter | From Russ White |
| Co. API | Co. Chevron |
| Dept. | Phone # 5102427038 |
| Fax # | Fax # |

Chevron

**Chevron Research and Technology Company**
1003 West Cutting Boulevard
P.O. Box 4054
Richmond, CA 94804-0054

**Toxicology & Health Risk Assessment**

March 18, 1996

Dr. Robert Barter
American Petroleum Institute
1220 L Street, NW
Washington, DC 20005

RE: CONTRACT MODIFICATION FOR HES1860-L-00870-BLEND, "FUEL BLENDING, HEADSPACE ANALYSIS, AND BENCHTOP VAPOR GENERATION FOR AN ALTERNATIVE EVAPORATIVE EMISSIONS GENERATION PROCEDURE UNDER CLEAN AIR ACT SECTION 211(b)."

Dear Dr. Barter:

Attached are the revised cost estimates for the API project, HES1860-L-00870-BLEND. The additional costs ($9,740) are due to the extra time and equipment required to validate a method to determine the composition of the equilibrium headspace at 130F. The methodology proposed in the original bid gave extremely poor reproducibility. The use of a gas-tight syringe to inject the headspace sample was eventually abandoned in favor of an automated gas-sampling instrument that was in storage at Chevron Research. Since the equilibrium composition at 130F is the EPA's benchmark to compare alternative vapor generation methods, it was critical to establish a reliable method. The new method provides the precision needed to complete this phase of the project.

Please contact me at (510) 242-7038 if there are any questions about this contract modification.

Sincerely,

Russell White

Russell White

Enclosure: 1

cc: R. M. Angus, P. W. Beatty, J. M. Hubert, G. Hemighaus, files

| | | | | | |
|---|---|---|---|---|---|
| REVISED COST ESTIMATES -- MARCH 18, 1996 | | | | | |
| CAA 211(b) FUEL BLENDING, HEADSPACE ANALYSIS, AND BENCHTOP VAPOR GENERATIONS | | | | | |
| FUEL BLENDING -- 10 gallon sample | | | | 18-Mar-96 | |
| | | | $ Cost Estimate | Revised Costs | |
| 94-02 Gasoline from API | | | 0 | | |
| MTBE | 8 liters from Aldrich - 99.8% | | 130 | | |
| TAME | 2 gallons from Chevron - 98.9% | | 0 | | |
| DIPE | 8 liters from Aldrich - 98% | | 172 | | |
| ETBE | 5 gal from Phillips - 98.7% | | 325 | | |
| EtOH | 1 gallon from Gold Shield -100% | | 0 | | |
| TBA | 8 liters from Aldrich - 99.5% | | 208 | | |
| Blending and Supplies | | | 1000 | | |
| 7 GCs on blends (SE-30) | | | 1855 | | |
| 7 RVPs on blends (ASTM D519) | | | 315 | | |
| 7 Boiling Curves on blends (ASTM D86) | | | 280 | | |
| 6 Fuel Oxygen on blends (ASTM D4815) | | | 1050 | | |
| HEADSPACE ANALYSIS | | | | | |
| GC Lab Setup | | | 1000 | | 10,740 |
| Samples at 130 F -- duplicate GC analysis | | | 3710 | | |
| BENCHTOP VAPOR GENERATIONS | | | | | |
| 8 Vapor Generations | | | 9600 | | |
| 8 GCs for 130 F vapor temp sample | | | 2120 | | |
| 8 GCs for 15 vol.% sample | | | 2120 | (if necessary) | |
| Project Management | | | 5000 | (50 hours at $100) | |
| QA | | | 2600 | (40 hours at $65) | |
| | | TOTAL $ | 31485 | | 41225 |

American Petroleum Institute

1220 L Street, Northwest
Washington, D.C. 20005-4070
202-682-8000

MEMORANDUM

TO: Russ White
Chevron Research and Technology

FROM: CeCe Sharp
Research Group Administrator

DATE: April 10, 1996

RE: Enclosed Contract Amendment

Enclosed are **two** executed copies of the amendment to Chevron's contract with the Section 211(b) Research Group for **"Fuel Blending, Headspace analysis and Benchtop Vapor Generation..."**

Please have them executed by the appropriate person and return **one** fully executed agreement to me in the enclosed envelope.

Please feel free to call me at (202) 682-8333 if you have questions.

Thanks.

cc: D. Mongillo (w/o enclosure)
R. Barter (w/o enclosure)

Sponsor:

American Petroleum Institute
Washington, D. C.

Study Title:

# Fuel Blending, Headspace Analysis, and Benchtop Vapor Generation for an Alternative Evaporative Emissions Generation Procedure Under Clean Air Act Section 211(b)

Date:

November 15, 1995

Performing Laboratory:

Chevron Research and Technology Company
100 Chevron Way
Richmond, CA 94802

Laboratory Project Identification:

API _____

## STUDY IDENTIFICATION

Fuel Blending, Headspace Analysis, and Benchtop Vapor Generation for an Alternative Evaporative Emissions Generation Procedure Under Clean Air Act Section 211(b)

| | |
|---|---|
| Test Substances: | API 94-02 Gasoline<br>API 94-02 Gasoline/MTBE Blend<br>API 94-02 Gasoline/Ethanol Blend<br>API 94-02 Gasoline/TAME Blend<br>API 94-02 Gasoline/ETBE Blend<br>API 94-02 Gasoline /DIPE Blend<br>API 94-02 Gasoline/TBA Blend |
| Sponsor: | American Petroleum Institute<br>1220 L Street, N. W.<br>Washington, D. C. 20005 |
| Sponsor's Representative: | Robert Barter<br>Telephone: 202-682-8342 |
| Sponsor's Alternate Representative: | Ce Ce Sharp<br>Telephone: 202-682-8333 |
| Study Director: | Russell White<br>Telephone: 510-242-7038 |
| Testing Facility: | Chevron Research and Technology Company<br>Analytical Sciences Unit (ASU)<br>Toxicology and Health Risk Assessment (THRA)<br>100 Chevron Way<br>Richmond, CA 94802 |

Proposed Study Timetable

| | |
|---|---|
| Experimental Start Date: | Week of December 4, 1995 |
| Experimental Termination Date: | Week of February 26, 1996 |
| Draft Report Date: | Week of March 4, 1996 |

1. Study Title: Fuel Blending, Headspace Analysis, and Benchtop Vapor Generation for an Alternative Evaporative Emissions Generation Procedure Under Clean Air Act Section 211(b).

2. Purpose: To develop data to support a petition for a change in the method of evaporative emissions generation under Clean Air Act Section 211(b).

3. Regulatory Compliance: This study will be conducted in the spirit of EPA Good Laboratory Practice Regulations set forth in Part 792 (TSCA) of Title 40 of the Code of Federal Regulations.

4. Quality Assurance: The protocol, one in-life phase, and the final report will be audited by the ASU Quality Assurance Unit in accordance with the ASU Standard Operating Procedures (SOPs) and policies.

5. Test Materials:

A. Identification: Six samples of API 94-02 Gasoline Lot S-424-A from Phillips 66 Company will be separately blended with the following materials as determined in Section 7, Experimental Design;

- Methyl Tertiary Butyl Ether (CAS 1634-04-4) from Aldrich Chemical
- Ethyl Alcohol (CAS 64-17-5) from Gold Shield Chemical
- Tertiary Amyl Methyl Ether (CAS 944-05-8) from Chevron Research
- Ethyl Tertiary Butyl Ether (CAS 637-92-3) from Phillips Petroleum
- Tertiary Butyl Alcohol (CAS 75-65-0) from Aldrich Chemical
- Diisopropyl Ether (CAS 108-20-3) from Aldrich Chemical

B. Purity and Stability: The Sponsor assumes responsibility for the composition and stability of API 94-02 Gasoline. All other materials will be obtained by Chevron and will be "chemical" grade or better as specified in the 211(b) rule. The purity of these materials will be based on information from the commercial vendors or determined by gas chromatography analysis by Chevron. No stability studies will be done.

C. Storage: The materials and blends will normally be stored at ambient temperature. As appropriate, the materials and blends will be chilled prior to use.

D. Inventory: The materials and blends will be stored in the original containers, or in the equivalent thereof, or in 5 gallon steel cans.

E. Sample Retention: If desired by the Sponsor, the remaining blended gasoline will be sent to the Sponsor's Repository for archiving at the termination of the study.

F. Safety Precautions: Material Safety Data Sheets will be available for the base gasoline and each oxygenate. General safety precautions as required by the laboratory's policies and procedures will be followed. Any questions of toxicity related to accidental exposure will be referred to the Chevron Emergency Information Center at 800-231-0623.

6. Test System: Not applicable.

7. Experimental Design:

A. Fuel Sample Blending: (ASU SOP ME-###-#). Each oxygenate will be blended with API 94-02 gasoline by weight to achieve a final weight of 28387.5 grams (this would be the weight of 10 gallons of API 94-02 at 60F). The fuel oxygen content of each blend will be determined by ASTM D4815-94a. Other fuel inspections will include Reid vapor pressure (ASTM D519), boiling curve (ASTM D86), and gas chromatography for identification of components (Chevron SE-30).

| | % Oxygen per Molecule | Finished Blend Wt. (grams) | Finished Wt% O Target | Oxygen Needed (grams) | Oxygenate Needed (grams) | Finished Blend Wt.% Oxygenate* | Gasoline Needed (grams) |
|---|---|---|---|---|---|---|---|
| | | | | | | | |
| MTBE | 18.2 | 28387.5 | 2.7 | 766.5 | 4211.5 | 14.84 ± 0.73 | 24176 |
| TAME | 15.7 | 28387.5 | 2.7 | 766.5 | 4882.2 | 17.20 ± 1.32 | 23505.3 |
| DIPE | 15.7 | 28387.5 | 2.7 | 766.5 | 4882.2 | 17.20 ± 2.83 | 23505.3 |
| ETBE | 15.7 | 28387.5 | 2.7 | 766.5 | 4882.2 | 17.20 ± 3.13 | 23505.3 |
| EtOH | 34.8 | 28387.5 | 3.7 | 1050.4 | 3018.2 | 10.63 ± 0.88 | 25369.3 |
| TBA | 21.6 | 28387.5 | 3.7 | 1050.4 | 4862.9 | 17.13 ± 1.27 | 23524.6 |
| API 94-02 | 0 | 28387.5 | 0 | 0 | 0 | 0 | 28387.5 |
| | | | | | | | |
| * Reproducibility determined from ASTM D4815-94a. Assumes oxygenate purity of 100%. | | | | | | | |

B. Headspace Analysis by Gas Chromatography: (ASU SOP ME-###-#). In turn, 8 milliliters of API 94-02 gasoline and each of the oxygenate blends from Part A will be put into 20 milliliter headspace vials. This volume is consistent with the current CAA 211(b) rule requirement of an "evaporative emission generator" being 40% full at the start of the procedure. They will be stored refrigerated until needed. The appropriate vial will be placed in a waterbath maintained at 130°F plus or minus 1°F. After 15 minutes the sample vial will be inverted several times and replaced in the waterbath for 10 minutes more. A sample of the headspace will be withdrawn with a gastight syringe (at 130°F) and injected into a gas chromatograph following Chevron procedure SE-30. A duplicate sample will be done on the same day.

C. Benchtop Vapor Generation: (ASU SOP ME-###-#). In turn, twenty liters (5.3 gallons) of each blend will be put into a fifty liter (13.2 gallon) distillation flask with a two inch sample port. This volume is consistent with the current CAA 211(b) rule requirement of an "evaporative emission generator" being 40% full at the start of the procedure. The vapor passes out the port opening through a 6-inch glass riser attached to a 20-inch diagonal glass condenser and two sequential "overhead" cold traps. The condenser, collection vessel, and overhead traps are chilled with a dry ice-alcohol mixture. The sample will be mixed and slowly heated to bring the vapor temperature to 130°F. Monitoring of the liquid and vapor temperatures will be done continuously and recorded on the distillation run log as appropriate. If the volume of vapor condensate collected when 130°F vapor temperature is reached is less than three liters (15% of starting volume), the first collection sample will be removed and heating will continue until a second sample is collected to achieve a total volume collected of approximately three liters. Both samples (if necessary) will

be analyzed by gas chromatography (Chevron SE-30). API 94-02 gasoline will also be used in this procedure with a starting volume of forty liters (10.6 gallons) to compare the impact of different starting volumes on vapor condensate composition.

D. Statistical Analyses: No statistical analyses are required. Summary tables will be prepared to facilitate read across comparisons between the blended gasoline liquid sample, the headspace vapor composition, and the vapor generation condensate composition. Approximately 40 individual components including the appropriate oxygenate and carbon numbers C2 to C9 will be summarized. Electronic copies of the summary tables (Microsoft Excel 5.0a) will be sent to the sponsor.

8. Report: A draft final report audited by ASU's Quality Assurance Unit will be sent to the Sponsor's Representative for review. Four copies of the approved final report will be submitted to the Sponsor. The final report will include, but not be limited to the following information:

- Introduction
- A copy of the protocol, all protocol amendments, and all protocol deviations and their effects on the study
- Summary of results
- Copies of raw data

9. Records to be Maintained: All raw data, or copies thereof, will be available at CRTC to facilitate auditing the study during its progress and before acceptance of the final report. When the final report is completed, all raw data, samples (if desired), and final report will be sent to the Sponsor.

10. Study Design Alteration: No alterations will be made to this protocol without written approval from the Sponsor. Written approval will be in the form of an amendment that is to be attached to the final protocol. In the event an immediate alteration required, the change shall be made and documented by the Study Director after seeking verbal approval from the Sponsor's Representative or Alternate. Written approval in the form of an amendment to the protocol will follow and be attached to the final protocol.

PROTOCOL APPROVAL

| | |
|---|---|
| Sponsor's Representative<br>American Petroleum Institute | Date |
| Study Director<br>Chevron Research and Technology Company | Date |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **CAA 211(b) FUEL BLENDING, HEADSPACE ANALYSIS, AND BENCHTOP VAPOR GENERATIONS** | | | | | | | |
| | | | | | | | |
| **FUEL BLENDING -- 10 gallon sample** | | | | | | | |
| | | | | $ Cost Estimate | | | |
| 94-02 Gasoline from API | | | | 0 | | | |
| MTBE | 8 liters from Aldrich - 99.8% | | | 130 | | | |
| TAME | 2 gallons from Chevron - >98% | | | 0 | | | |
| DIPE | 8 liters from Aldrich - 98% | | | 172 | | | |
| ETBE | 5 gal from Phillips - 98.7% | | | 325 | | | |
| EtOH | 1 gallon from Gold Shield -100% | | | 0 | | | |
| TBA | 8 liters from Aldrich - 99.5% | | | 208 | | | |
| | | | | | | | |
| Blending and Supplies | | | | 1000 | | | |
| 7 GCs on blends (SE-30) | | | | 1855 | | | |
| 7 RVPs on blends (ASTM D519) | | | | 315 | | | |
| 7 Boiling Curves on blends (ASTM D86) | | | | 280 | | | |
| 6 Fuel Oxygen on blends (ASTM D4815) | | | | 1050 | | | |
| | | | | | | | |
| | | | | | | | |
| **HEADSPACE ANALYSIS** | | | | | | | |
| GC Lab Setup | | | | 1000 | | | |
| Samples at 130 F -- duplicate GC analysis | | | | 3710 | | | |
| | | | | | | | |
| | | | | | | | |
| **BENCHTOP VAPOR GENERATIONS** | | | | | | | |
| 8 Vapor Generations | | | | 9600 | | | |
| 8 GCs for 130 F vapor temp sample | | | | 2120 | | | |
| 8 GCs for 15 vol.% sample | | | | 2120 | (if necessary) | | |
| | | | | | | | |
| | | | | | | | |
| **Project Management** | | | | 5000 | (50 hours at $100) | | |
| **QA** | | | | 2600 | (40 hours at $65) | | |
| | | | TOTAL $ | 31485 | | | |
| | | | | | | | |

**American Petroleum Institute**
1220 L Street, Northwest
Washington, D.C. 20005
(202) 682-8240

G. William Frick
Vice President
Health, Environment and Safety

December 29, 1995

John C. Sebastian
Chevron Research and Technology Company
100 Chevron Way
Richmond, CA 94802

Dear Mr. Sebastian:

This letter of Agreement between the American Petroleum Institute (API) and Chevron Research and Technology Company, Analytical Sciences Unit, Toxicology and Health Risk Assessment (Chevron), authorizes Chevron to conduct a study entitled: "***Fuel Blending, Headspace Analysis, and Benchtop Vapor Generation for an Alternative Evaporative Emissions Generation Procedure Under Clean Air Act Section 211(b).***" The study shall be performed in accordance with Chevron's protocol dated November 15, 1995 a copy of which is attached hereto and made a part hereof. This Agreement is subject to the following terms and conditions:

1. This project shall be designated HES1860-L-00870-BLEND (such designation ***must*** appear on all invoices and other correspondence relating to this project) and shall be conducted by Chevron Research and Technology (Russell White, Ph.D., shall be the study director). Both parties acknowledge that the services rendered by Chevron hereunder are of a special and unique nature to Chevron and are of the essence of this Agreement. Neither Chevron nor the API may assign this Agreement or its right or obligations hereunder without the prior written consent of the other party, except that Chevron may assign this project to another Chevron entity wholly owned by the Chevron Corporation. Any delegation, assignment, or transfer by either party of its rights hereunder, except as herein above provided, without the prior written consent of the other party shall be void.

2. Chevron agrees to perform all its obligations hereunder for an amount not-to-exceed thirty-one thousand four hundred eighty-five dollars ($31,485). Chevron shall invoice API upon receipt of final report. API may withhold up to fifteen percent (15%) of the Agreement amount, pending API's acceptance of all work products as specified in Chevron's attached protocol.

3. Chevron shall submit two (2) copies of a draft final report, to API for review and comment no later than three (3) weeks after the completion of laboratory work. Within twenty-one (21) days of receipt of API comments on the draft final report, Chevron shall provide API with three (3) copies of a final report.

4. Chevron shall not use the trademark or name of the American Petroleum Institute, or any abbreviation thereof, in any publicity, advertising or for other promotional purposes without the prior written approval of API.

5. Any discoveries or inventions resulting solely from the conduct of the work described herein shall be dedicated to the public.

6. Upon request of API, Chevron agrees to support its work hereunder and to offer testimony thereon to governmental bodies (legislative, executive or judicial). Expenses for such services shall be paid by API at Chevron's billing rates in effect at the time such services are rendered in addition to out of pocket expenses.

7. It is agreed that API shall have the right to terminate this Agreement at any time by giving notice of termination to Chevron. Upon receipt of such notice of termination, Chevron shall cease incurring costs on this project except with the prior approval of API for such costs as are necessary to close out the project. In the event of such termination, API's sole obligation will be to reimburse Chevron for actual costs incurred as of the date of notice of termination, and any subsequent costs incurred with prior approval of API, including all of Chevron's legal commitments to third parties for activities under this Agreement. In no event shall such payment exceed the maximum amount of the Agreement as set forth in paragraph 2.

8. In the event of inconsistencies between the terms of this Agreement and the attachment hereto, the express terms of this Agreement shall govern.

9. This Agreement shall become effective upon Chevron's signature below and terminate upon API's acceptance of all work products specified in Chevron's attached protocol.

10. It is understood that Chevron is acting as an independent contractor in its performance of any and all work hereunder.

11. Administrative aspects of this Agreement shall be under the direction of Robert T. Drew, Ph.D. (or his designated representative), American Petroleum Institute, 1220 L Street, NW, Washington, DC 20005. The designated representative under this Agreement shall be Robert Barter, Ph.D. All correspondence and reports relating to work conducted hereunder, shall be directed to the attention of Dr. Barter at the foregoing address and to such other individuals as specified by API.

12. NO CHANGE, MODIFICATION, EXTENSION, TERMINATION, OR WAIVER OF THIS AGREEMENT OR ANY OF THE PROVISIONS HEREOF SHALL BE EFFECTIVE UNLESS MADE IN WRITING AND SIGNED BY A DULY AUTHORIZED OFFICER OF THE PARTY AGAINST WHOM IT IS SOUGHT TO BE ENFORCED. CHANGES BINDING ON API MUST BE IN WRITING AND SIGNED BY THE API OFFICIAL WHO, AT THE TIME OF SAID CHANGE, OCCUPIES THE POSITION OF EXECUTIVE VICE PRESIDENT, AMERICAN PETROLEUM INSTITUTE, OR HIS DESIGNEE. CHEVRON UNDERSTANDS AND AGREES THAT API IS NOT RESPONSIBLE FOR WORK PERFORMED, OR COSTS INCURRED, WITHOUT THE EXPRESS WRITTEN AUTHORIZATION OF THE EXECUTIVE VICE PRESIDENT OF API OR HIS DESIGNEE.

13. Paragraphs 4-8 and 10-13 shall survive the termination of this Agreement.

If the above terms and conditions are acceptable, please sign below and return one copy of this Agreement to API.

CHEVRON RESEARCH AND TECHNOLOGY COMPANY

BY: John C. Sebastian
John C. Sebastian.

DATE: January 8, 1996

AMERICAN PETROLEUM INSTITUTE

BY: G. William Frick
G. William Frick
Vice President, Health, Environment and Safety

BY: Del Persinger
Del Persinger
Assistant Secretary

DATE: December 29, 1995

Sponsor:

American Petroleum Institute
Washington, D. C.

Study Title:

# Fuel Blending, Headspace Analysis, and Benchtop Vapor Generation for an Alternative Evaporative Emissions Generation Procedure Under Clean Air Act Section 211(b)

Date:

November 15, 1995

Performing Laboratory:

Chevron Research and Technology Company
100 Chevron Way
Richmond, CA 94802

Laboratory Project Identification:

API _____

## STUDY IDENTIFICATION

Fuel Blending, Headspace Analysis, and Benchtop Vapor Generation for an Alternative Evaporative Emissions Generation Procedure Under Clean Air Act Section 211(b)

| | |
|---|---|
| Test Substances: | API 94-02 Gasoline<br>API 94-02 Gasoline/MTBE Blend<br>API 94-02 Gasoline/Ethanol Blend<br>API 94-02 Gasoline/TAME Blend<br>API 94-02 Gasoline/ETBE Blend<br>API 94-02 Gasoline /DIPE Blend<br>API 94-02 Gasoline/TBA Blend |
| Sponsor: | American Petroleum Institute<br>1220 L Street, N. W.<br>Washington, D. C. 20005 |
| Sponsor's Representative: | Robert Barter<br>Telephone: 202-682-8342 |
| Sponsor's Alternate Representative: | Ce Ce Sharp<br>Telephone: 202-682-8333 |
| Study Director: | Russell White<br>Telephone: 510-242-7038 |
| Testing Facility: | Chevron Research and Technology Company<br>Analytical Sciences Unit (ASU)<br>Toxicology and Health Risk Assessment (THRA)<br>100 Chevron Way<br>Richmond, CA 94802 |

Proposed Study Timetable

| | |
|---|---|
| Experimental Start Date: | Week of December 4, 1995 |
| Experimental Termination Date: | Week of February 26, 1996 |
| Draft Report Date: | Week of March 4, 1996 |

1. Study Title: Fuel Blending, Headspace Analysis, and Benchtop Vapor Generation for an Alternative Evaporative Emissions Generation Procedure Under Clean Air Act Section 211(b).

2. Purpose: To develop data to support a petition for a change in the method of evaporative emissions generation under Clean Air Act Section 211(b).

3. Regulatory Compliance: This study will be conducted in the spirit of EPA Good Laboratory Practice Regulations set forth in Part 792 (TSCA) of Title 40 of the Code of Federal Regulations.

4. Quality Assurance: The protocol, one in-life phase, and the final report will be audited by the ASU Quality Assurance Unit in accordance with the ASU Standard Operating Procedures (SOPs) and policies.

5. Test Materials:

A. Identification: Six samples of API 94-02 Gasoline Lot S-424-A from Phillips 66 Company will be separately blended with the following materials as determined in Section 7, Experimental Design;

- Methyl Tertiary Butyl Ether (CAS 1634-04-4) from Aldrich Chemical
- Ethyl Alcohol (CAS 64-17-5) from Gold Shield Chemical
- Tertiary Amyl Methyl Ether (CAS 944-05-8) from Chevron Research
- Ethyl Tertiary Butyl Ether (CAS 637-92-3) from Phillips Petroleum
- Tertiary Butyl Alcohol (CAS 75-65-0) from Aldrich Chemical
- Diisopropyl Ether (CAS 108-20-3) from Aldrich Chemical

B. Purity and Stability: The Sponsor assumes responsibility for the composition and stability of API 94-02 Gasoline. All other materials will be obtained by Chevron and will be "chemical" grade or better as specified in the 211(b) rule. The purity of these materials will be based on information from the commercial vendors or determined by gas chromatography analysis by Chevron. No stability studies will be done.

C. Storage: The materials and blends will normally be stored at ambient temperature. As appropriate, the materials and blends will be chilled prior to use.

D. Inventory: The materials and blends will be stored in the original containers, or in the equivalent thereof, or in 5 gallon steel cans.

E. Sample Retention: If desired by the Sponsor, the remaining blended gasoline will be sent to the Sponsor's Repository for archiving at the termination of the study.

F. Safety Precautions: Material Safety Data Sheets will be available for the base gasoline and each oxygenate. General safety precautions as required by the laboratory's policies and procedures will be followed. Any questions of toxicity related to accidental exposure will be referred to the Chevron Emergency Information Center at 800-231-0623.

6. Test System: Not applicable.

7. Experimental Design:

A. Fuel Sample Blending: (ASU SOP ME-###-#). Each oxygenate will be blended with API 94-02 gasoline by weight to achieve a final weight of 28387.5 grams (this would be the weight of 10 gallons of API 94-02 at 60F). The fuel oxygen content of each blend will be determined by ASTM D4815-94a. Other fuel inspections will include Reid vapor pressure (ASTM D519), boiling curve (ASTM D86), and gas chromatography for identification of components (Chevron SE-30).

| | % Oxygen per Molecule | Finished Blend Wt. (grams) | Finished Wt% O Target | Oxygen Needed (grams) | Oxygenate Needed (grams) | Finished Blend Wt.% Oxygenate* | Gasoline Needed (grams) |
|---|---|---|---|---|---|---|---|
| MTBE | 18.2 | 28387.5 | 2.7 | 766.5 | 4211.5 | 14.84 ± 0.73 | 24176 |
| TAME | 15.7 | 28387.5 | 2.7 | 766.5 | 4882.2 | 17.20 ± 1.32 | 23505.3 |
| DIPE | 15.7 | 28387.5 | 2.7 | 766.5 | 4882.2 | 17.20 ± 2.83 | 23505.3 |
| ETBE | 15.7 | 28387.5 | 2.7 | 766.5 | 4882.2 | 17.20 ± 3.13 | 23505.3 |
| EtOH | 34.8 | 28387.5 | 3.7 | 1050.4 | 3018.2 | 10.63 ± 0.88 | 25369.3 |
| TBA | 21.6 | 28387.5 | 3.7 | 1050.4 | 4862.9 | 17.13 ± 1.27 | 23524.6 |
| API 94-02 | 0 | 28387.5 | 0 | 0 | 0 | 0 | 28387.5 |

* Reproducibility determined from ASTM D4815-94a. Assumes oxygenate purity of 100%.

B. Headspace Analysis by Gas Chromatography: (ASU SOP ME-###-#). In turn, 8 milliliters of API 94-02 gasoline and each of the oxygenate blends from Part A will be put into 20 milliliter headspace vials. This volume is consistent with the current CAA 211(b) rule requirement of an "evaporative emission generator" being 40% full at the start of the procedure. They will be stored refrigerated until needed. The appropriate vial will be placed in a waterbath maintained at 130°F plus or minus 1°F. After 15 minutes the sample vial will be inverted several times and replaced in the waterbath for 10 minutes more. A sample of the headspace will be withdrawn with a gastight syringe (at 130°F) and injected into a gas chromatograph following Chevron procedure SE-30. A duplicate sample will be done on the same day.

C. Benchtop Vapor Generation: (ASU SOP ME-###-#). In turn, twenty liters (5.3 gallons) of each blend will be put into a fifty liter (13.2 gallon) distillation flask with a two inch sample port. This volume is consistent with the current CAA 211(b) rule requirement of an "evaporative emission generator" being 40% full at the start of the procedure. The vapor passes out the port opening through a 6-inch glass riser attached to a 20-inch diagonal glass condenser and two sequential "overhead" cold traps. The condenser, collection vessel, and overhead traps are chilled with a dry ice-alcohol mixture. The sample will be mixed and slowly heated to bring the vapor temperature to 130°F. Monitoring of the liquid and vapor temperatures will be done continuously and recorded on the distillation run log as appropriate. If the volume of vapor condensate collected when 130°F vapor temperature is reached is less than three liters (15% of starting volume), the first collection sample will be removed and heating will continue until a second sample is collected to achieve a total volume collected of approximately three liters. Both samples (if necessary) will

be analyzed by gas chromatography (Chevron SE-30). API 94-02 gasoline will also be used in this procedure with a starting volume of forty liters (10.6 gallons) to compare the impact of different starting volumes on vapor condensate composition.

D. Statistical Analyses: No statistical analyses are required. Summary tables will be prepared to facilitate read across comparisons between the blended gasoline liquid sample, the headspace vapor composition, and the vapor generation condensate composition. Approximately 40 individual components including the appropriate oxygenate and carbon numbers C2 to C9 will be summarized. Electronic copies of the summary tables (Microsoft Excel 5.0a) will be sent to the sponsor.

8. Report: A draft final report audited by ASU's Quality Assurance Unit will be sent to the Sponsor's Representative for review. Four copies of the approved final report will be submitted to the Sponsor. The final report will include, but not be limited to the following information:

- Introduction
- A copy of the protocol, all protocol amendments, and all protocol deviations and their effects on the study
- Summary of results
- Copies of raw data

9. Records to be Maintained: All raw data, or copies thereof, will be available at CRTC to facilitate auditing the study during its progress and before acceptance of the final report. When the final report is completed, all raw data, samples (if desired), and final report will be sent to the Sponsor.

10. Study Design Alteration: No alterations will be made to this protocol without written approval from the Sponsor. Written approval will be in the form of an amendment that is to be attached to the final protocol. In the event an immediate alteration required, the change shall be made and documented by the Study Director after seeking verbal approval from the Sponsor's Representative or Alternate. Written approval in the form of an amendment to the protocol will follow and be attached to the final protocol.

PROTOCOL APPROVAL

| | |
|---|---|
| Sponsor's Representative<br>American Petroleum Institute | Date |
| Study Director<br>Chevron Research and Technology Company | Date |

| | | | |
|---|---|---|---|
| CAA 211(b) FUEL BLENDING, HEADSPACE ANALYSIS, AND BENCHTOP VAPOR GENERATIONS | | | |
| | | | |
| FUEL BLENDING -- 10 gallon sample | | | |
| | | $ Cost Estimate | |
| 94-02 Gasoline from API | | 0 | |
| MTBE | 8 liters from Aldrich - 99.8% | 130 | |
| TAME | 2 gallons from Chevron - >98% | 0 | |
| DIPE | 8 liters from Aldrich - 98% | 172 | |
| ETBE | 5 gal from Phillips - 98.7% | 325 | |
| EtOH | 1 gallon from Gold Shield -100% | 0 | |
| TBA | 8 liters from Aldrich - 99.5% | 208 | |
| | | | |
| Blending and Supplies | | 1000 | |
| 7 GCs on blends (SE-30) | | 1855 | |
| 7 RVPs on blends (ASTM D519) | | 315 | |
| 7 Boiling Curves on blends (ASTM D86) | | 280 | |
| 6 Fuel Oxygen on blends (ASTM D4815) | | 1050 | |
| | | | |
| | | | |
| HEADSPACE ANALYSIS | | | |
| GC Lab Setup | | 1000 | |
| Samples at 130 F -- duplicate GC analysis | | 3710 | |
| | | | |
| | | | |
| BENCHTOP VAPOR GENERATIONS | | | |
| 8 Vapor Generations | | 9600 | |
| 8 GCs for 130 F vapor temp sample | | 2120 | |
| 8 GCs for 15 vol.% sample | | 2120 | (if necessary) |
| | | | |
| | | | |
| Project Management | | 5000 | (50 hours at $100) |
| QA | | 2600 | (40 hours at $65) |
| | TOTAL $ | 31485 | |
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