EPA 909/9-81-004

ANALYSIS OF POTENTIAL METHODS TO DETERMINE VOLATILITIES OF HEAVY CRUDE OILS

DECEMBER 1981

FINAL REPORT

U. S. ENVIRONMENTAL PROTECTION AGENCY
REGION IX
215 FREMONT STREET
SAN FRANCISCO, CALIFORNIA 94105

EPA 909/9-81-004
December 1981

ANALYSIS OF POTENTIAL METHODS TO DETERMINE VOLATILITIES OF HEAVY CRUDE OILS

by:

Robert J. Bryan
ENGINEERING-SCIENCE

Contract No. 68-02-3509
Work Assignment No. 11

Project Officer:

Don Harvey

Prepared for:

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION IX
215 FREMONT STREET
SAN FRANCISCO, CALIFORNIA 94105

December 1981

ENGINEERING-SCIENCE
125 West Huntington Drive
Arcadia, California 91006

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SECTION 1

INTRODUCTION

This project, titled "Analysis of Potential Methods to Determine the Volatilities of Heavy Crude Oils", was conducted under Contract No. 68-02-3509, Work Assignment No. 11.

The purpose of the project was to screen alternatives for measuring the vapor pressure of heavy crude oils considering the cost of method development, equipment, and laboratory costs for using the developed method, repeatability, and the degree of conformity with API Nomograph results. Four alternatives including (1) extrapolation of the API nomograph, (2) measuring equilibrium vapor pressure, (3) using the Reid Method with modifications, and (4) measuring weight loss with time were to be initially considered. A method for measuring evaporation loss similar to (4) above was also to be studied for use in calculating evaporative emissions for open tanks and basins. Several other approaches to determining heavy crude oil vapor pressure were added to the list for preliminary evaluation.

SECTION 2

BACKGROUND

Compliance with the Clean Air Act Amendments of 1977 require that a number of states, including California, prepare and submit by July 1, 1982 a plan detailing the control measures which will be implemented to achieve attainment of the NAAQS for ozone by 1987. All such plans will depend heavily on comprehensive inventories of volatile organic compounds (VOCs) as a basis for determining the level of control of such emissions needed to attain compliance with the standard.

Compilation of an accurate VOC inventory will be necessary, but especially difficult, for those counties in California in which a substantial portion of such emissions emanates from crude oil production and associated storage and transfer. Determination of emissions from these sources requires the measurement of the volatility of the crude oil at the source temperature. This measurement in turn is dependent upon a knowledge of the "true vapor pressure" (TVP) of the crude oil.

Unfortunately, methods currently available for making such measurements (principally the Reid Vapor Pressure [RVP] method) are not satisfactory for measuring the TVP of crude oil because its normal source temperature is usually too high and its RVP too low. Therefore, estimates of emissions from sources associated with the production of crude oil are of questionable accuracy. Further, it is not possible to handle some high viscosity crudes at temperatures specified in the ASTM Method for RVP.

Several examples are cited to illustrate the problems associated with determining the vapor pressure of heavy crude oil or with use of vapor pressures to predict hydrocarbon emission losses from storage and transfer.

(1) In Kern County, California, an assumption is made for use in preparing the 1982 SIP revisions that all crude oil has the same vapor pressure as kerosene (reference personal communication between Larry Landis, Kern County APCD, and Stephanie Fullmer, Engineering-Science, Inc., April 20, 1981) While

this may be useful for preparing countywide emission inventory estimates, the assumption is based upon a limited number of vapor pressure-temperature plots. Further, there is a weakness in comparing a narrow boiling range product such as kerosene with unprocessed crude oils.

(2) The Second Edition of API Publication 2517, "Evaporation Loss from External Floating-Roof Tanks"[1], discusses the development of a product factor for use in their standing storage loss equation. The basis for this factor was data from pilot tank tests conducted with an octane/propane mixture, gasoline, and crude oil. It was found that after normalizing for differences in true vapor pressure and vapor molecular weight, crude oil losses were significantly lower than the octane/propane losses under the same conditions of seal configuration and wind speed. This was attributed to evaporation at non-equilibrium conditions, caused by the slower rate of migration of light ends from the bulk liquid to the liquid surface in crude oil as compared to the octane/propane mixture because the light ends migration rate is strongly viscosity dependent.

The average of crude oil losses to octane/propane losses was 0.4, with a range of 0.3 to 0.6. Therefore, it is obvious that factors other than the ability to obtain a reliable vapor pressure method for heavy crude oil must be considered in developing emission estimate procedures.

(3) Data on crude oil vapor pressures, hydrocarbon emissions during marine loading of crude oils, and composition of emissions were reported in a study conducted by Chevron Research Company for the Western Oil and Gas Association.[2] Vapor pressures were calculated from liquid compositional data using various vapor-equilibrium correlation procedures. In all cases these vapor pressures were higher than those predicted by the RVP-TVP correlation of API Bulletin 2514, "Hydrocarbon Emissions from Marine Vessel Loading of Gasolines", 1976. After recalculating on a methane and ethane free basis, the

vapor pressures obtained from vapor-liquid equilibrium procedures compared favorably with the API correlation of TVP with RVP for the total (methane and heavier) crude oil. This suggests that substantial amounts of light ends are lost during the sampling and analysis of crude oil for vapor pressure by the RVP method even when substantial care is taken. Also, the RVP procedure tends to slightly de-emphasize the influence of methane and ethane.

The emissions composition data obtained in the WOGA marine loading of crude oil study are also of interest. On the average, propane and heavier components comprised 95 weight percent of the hydrocarbon emissions. On a volume basis, the propane and components account for about 85 percent of the emissions. Therefore, volumetric vapor concentrations and thus vapor pressure can be significantly affected by methane and ethane content of crude oil. It follows that the value of vapor pressure as a predictor of emissions on a mass basis can be impaired by unknown variability in light ends because the mass concentration of hydrocarbon vapors present over crude oil is much less affected by light ends than is the volumetric concentration.

(4) Several studies in recent years have shown that hydrocarbon vapor concentration is not well correlated with various measures of crude oil vapor pressure. Engineering-Science (ES), in a study for the Western Oil and Gas Association[3], prepared an extrapolated version of the API TVP-RVP nomograph (Figure 1). This nomograph was used to determine TVP (according to the API terminology). The RVPs, TVPs, and a function of vapor pressure used in API Bulletin 2518 for prediction of breathing losses in fixed-roof tanks were all plotted versus measured hydrocarbon vapor concentrations. These plots are reproduced in Figures 2, 3, and 4. It is interesting to note while there is a good deal of scatter in all the plots, the RVP shows the highest correlation coefficient of the three parameters considered. It should be recognized,

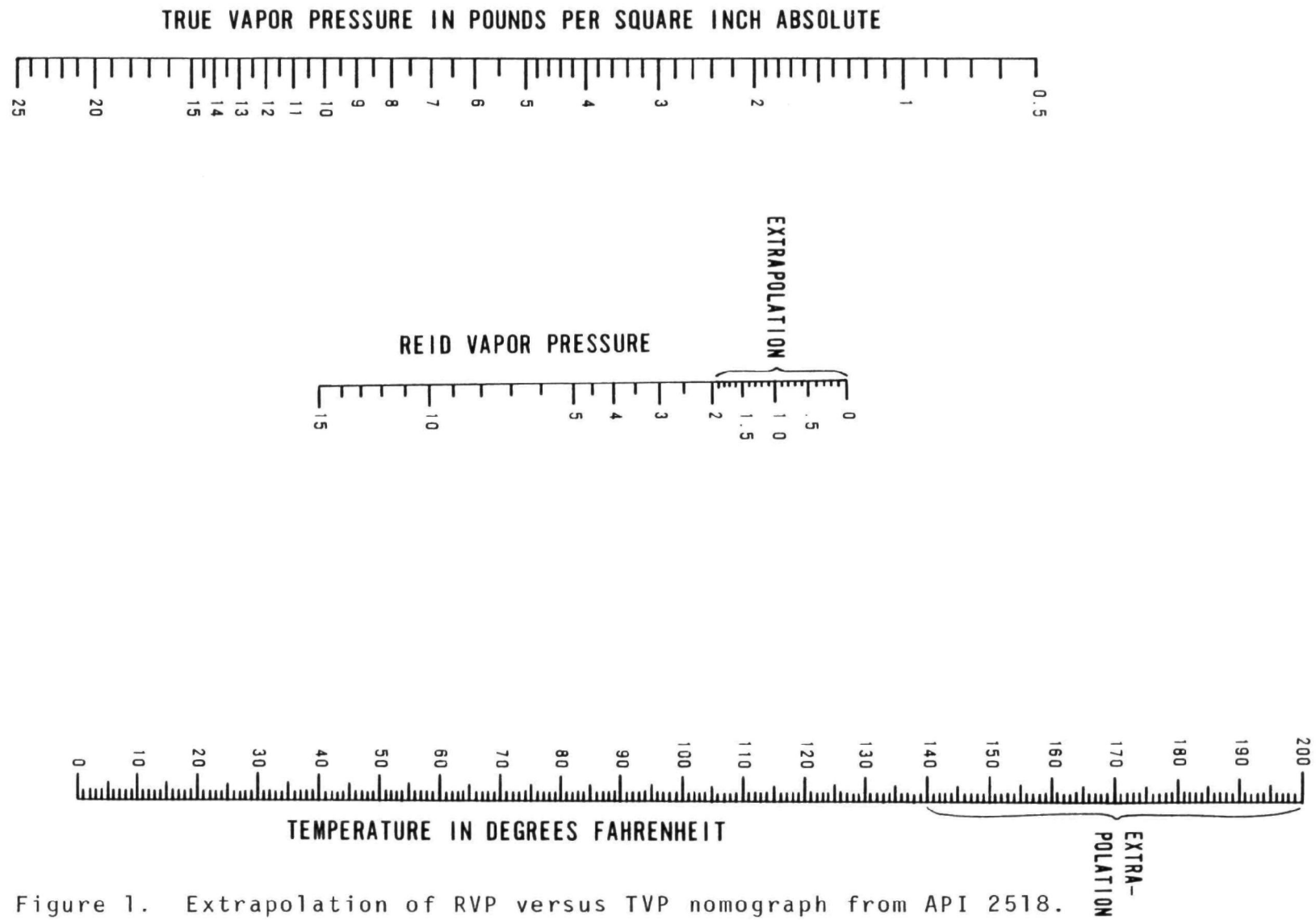

Figure 1. Extrapolation of RVP versus TVP nomograph from API 2518.

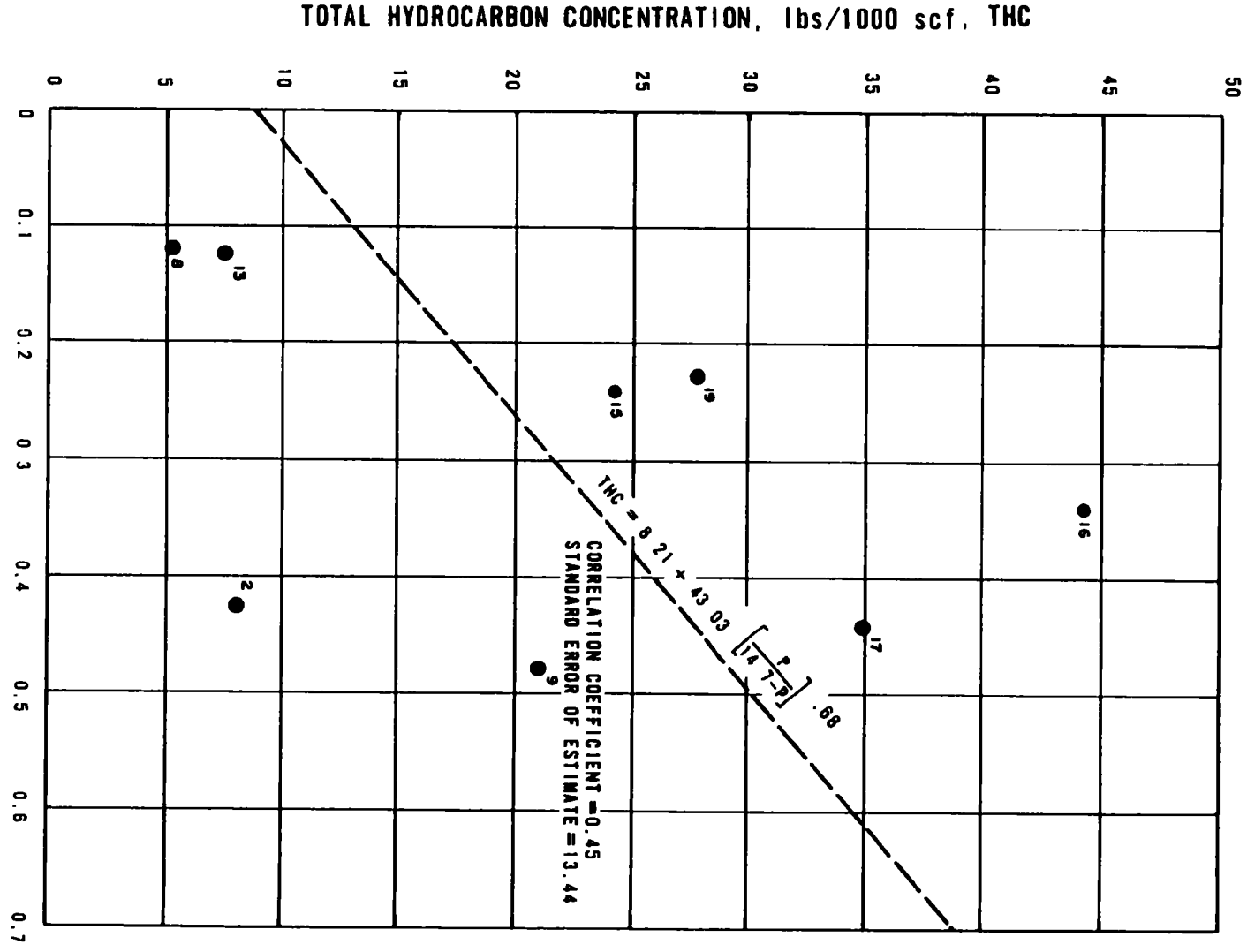

Figure 2. Hydrocarbon vapor concentration versus $\left[\frac{P}{14.7-P}\right]^{0.68}$ for crude oil standing storage tanks.

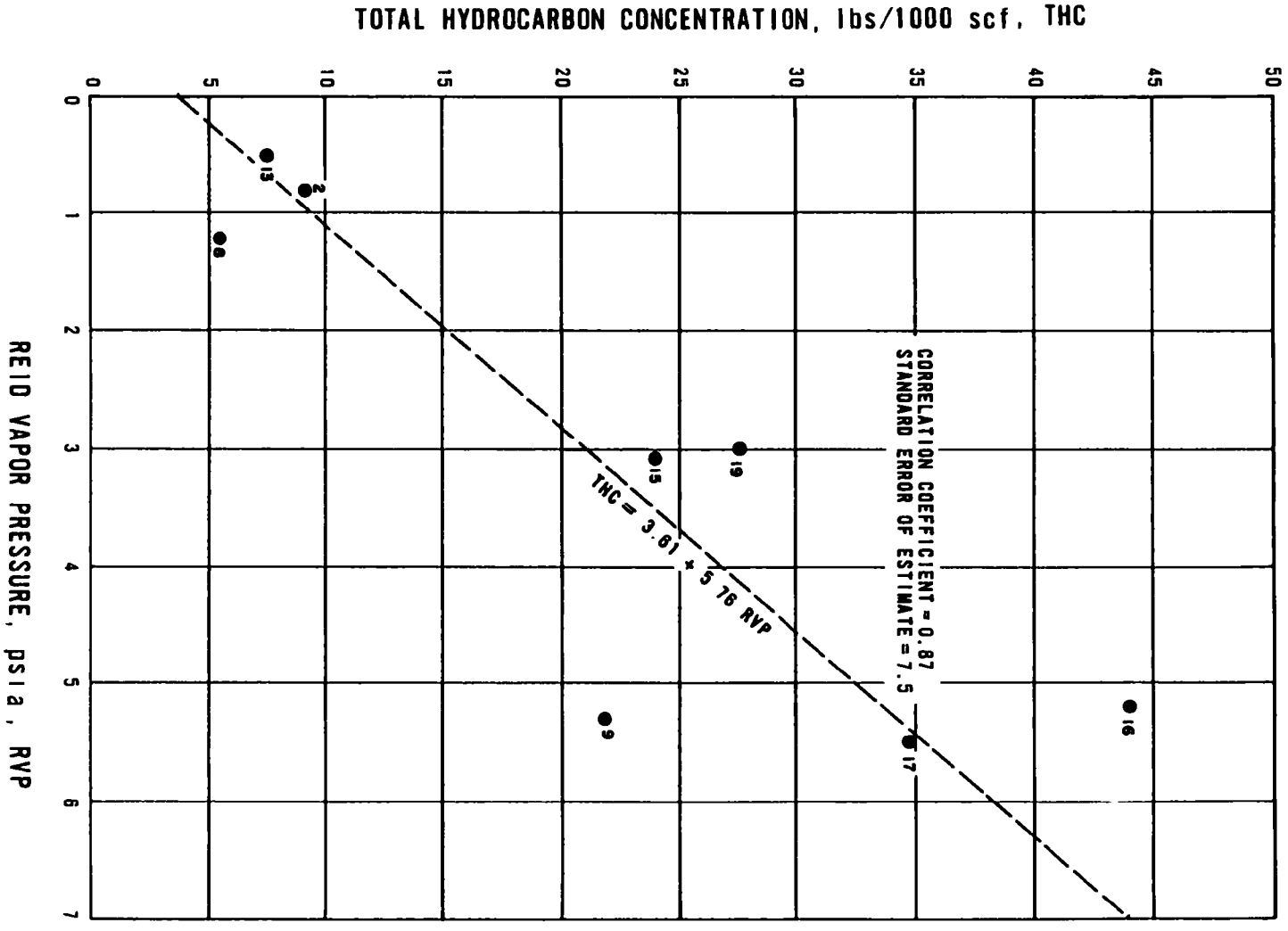

Figure 3. Emission concentration versus crude oil RVP, standing storage tanks.

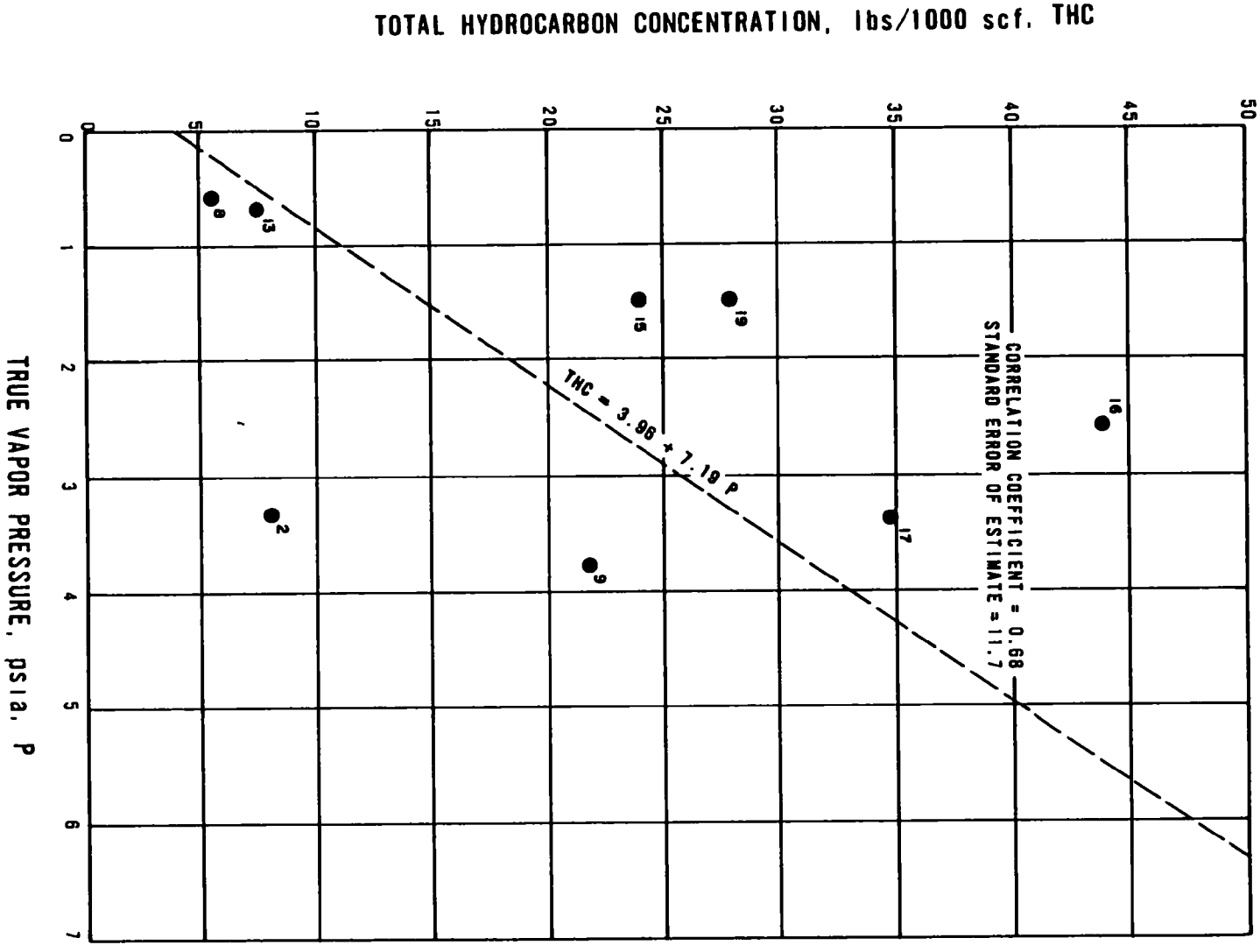

Figure 4. Emission concentration versus crude oil TVP, standing storage tanks.

however, that there are a number of factors other than vapor pressure which influence vapor concentration in a tank head space. These include approach to equilibrium, presence of leaks, and immediate tank history as to product characteristics.

(5) A special problem exists with unstabilized crudes. Crude oil from wells can be subjected to a number of treatments to separate gas, water, and contaminants from the crude oil. Operations are performed in oil/gas separators, heater treaters, free water knockout tanks, and wash tanks to name several of these process vessels. Some of these tanks may be pressurized, others are at or close to atmosphere pressures. In some situations the crude oil is hot enough for flashing to occur. In oil field tank operations conducted prior to custody transfer (the last transfer from the field to a means of transportation), then, it is quite possible for the concentration of light ends, and thus the vapor pressure, to change quite rapidly along the processing steps, and even with time in any given tank. This obviously complicates the problem of collecting representative crude oil samples. Further, when the crude oil is held at temperatures significantly above ambient temperature and turn-over is rapid, there exists a significant potential for temperature stratification in the tank, thus raising a question as to what temperature is to be selected for reporting true vapor pressure or other measure of volatility.

SECTION 3

APPROACH

This project was based upon review of literature and direct contact with knowledgeable persons in the field. No laboratory or field work was conducted. The project was divided into two phases. Phase I covered the screening of alternative methods for measuring the volatilities of heavy crude oils other than the four approaches specified in the Work Assignment. The principal alternatives reviewed during Phase I were methods which had been the subject of a staff study by the California Air Resources Board. Verbal suggestions were obtained from several petroleum industry sources which generally addressed the need for some technique to account for the influence of methane and ethane when measuring vapor pressure of crude oils. A report was submitted on the Phase I effort. Following submission of this report, a specific written procedure was submitted by Chevron Research Company for the determination of vapor composition and vapor pressure of heavy crude oils. This method was also considered.

The methods selected for further study were evaluated using the following criteria:

- Cost of method development
- Equipment and laboratory costs for using the developed method;
- Repeatability of the method
- Possible sources of error
- Degree of expected conformity with API Nomograph results
- Problems with use as a predictive parameter for hydrocarbon emissions
- Problems of field and laboratory use

As a result of this analysis, the methods were rated as candidates for further developmental work.

SECTION 4

DISCUSSION

This project is concerned with potential methods of determining the volatilities of heavy crude oils. Volatility is a term relating to the potential of a substance to evaporate. Vapor pressure is probably the most common measure of volatility but measures of evaporation such as distillation have also been used. Vapor pressure, for our purposes, is defined as a measure of the force that tends to volatilize any volatile liquid. This force is conventionally measured as pressure under specified conditions. The term "true vapor pressure" has a special meaning in multi-component mixtures because composition of the mixture will be changed as vaporization occurs and vapor pressure will be lowered concurrently. Thus, true vapor pressure of mixtures must be measured without vaporization taking place. This is difficult to carry out experimentally with a high degree of accuracy. True vapor pressure is also termed as the "bubble point" pressure.

Because of the experimental difficulties in directly determining true vapor pressures, the Reid Vapor Pressure (RVP) is most often used to express the vapor pressure of petroleum mixtures. The RVP is the absolute pressure in pounds per square inch determined at 100°F and V/L = 4 (ratio of vapor volume to liquid volume, as defined in ASTM Designation : D323-72) by using the apparatus and procedures as standardized under the auspices of the American Society for Testing Materials. Thus, the RVP represents the vapor pressure of a sample which has had its composition changed during the vaporization required to saturate the vapor space of the measuring apparatus.

Correlations have been developed relating true vapor pressure to Reid vapor pressure. These are prepared in the form of nomographs included in a number of American Petroleum Institute (API) publications.[4] For gasoline and finished petroleum products, the alignment charts include RVP, temperature, the slope of the ASTM distillation curve at the 10 percent point, and the "true vapor pressure". For crude oil, however, there is no provision for consideration of the

distillation curve slope. This alignment chart is limited to crude oils with RVPs above 2 psi and storage temperatures below 140°F. There is still another problem having to do with the use of ASTM Method D323-72 for RVP with some crude oils. This is the requirement that the sample container and its contents be cooled to 32 to 40°F before the container is opened and the contents transferred to the liquid chamber of the RVP bomb (a term for the apparatus). Some crude oils cannot be poured at these temperatures. The alternative methods for crude oil volatility considered in this project take into account one or more of the problems discussed previously. They include modifying the TVP-RVP nomograph to take into account distillation slope or gravity, methods of minimizing transfer loss, extending the applicable temperature and vapor pressure range, and determining the methane and ethane influence on vapor pressure.

Alternative Methods for Crude Oil Volatility Considered

Each of the alternative approaches considered as a measure of heavy crude oil volatility is discussed below. Some of the approaches are in the form of fairly detailed methods and some are conceptual only. Those in the former category are attached in the appendix to this report. Following the narrative discussion of the methods, a matrix chart rating the methods against certain evaluation criteria is given.

1. Extrapolation or Modification of the API Nomograph

   This approach would require the acquisition of more data on true vapor pressures versus Reid vapor pressures covering a variety of crude oils. Possibly the minimum RVP could be lowered and the temperature limit raised. This would extend the range of applicability but would not solve sampling, crude oil transfer, and light ends problems. It is possible that sufficient data could be obtained that ASTM distillation curve slope or API gravity could be included to refine the TVP-RVP nomograph. The Chairperson of the API Committee on Evaporation Loss, Karen Hanzevack of Exxon Research, stated (personal

communication with Robert Bryan of Engineering-Science, Inc., July 17, 1981) that the Committee is not satisfied with the existing crude oil nomograph and is collecting existing data on a wider range of crude oils. The intent would be to add a grid of lines for crudes of different API gravities as a substitute for the single correlation line in the current chart. The Chairperson further gave the opinion that no measure of volatility better than the RVP method has yet been developed. She believes field work is necessary to confirm the value of any revised procedure for vapor pressure determination.

The WOGA sponsored marine crude oil loading study also comments on this matter. Their report[2)] states that an alignment grid which includes both temperatures and slope of the ASTM distillation curve or API gravity would improve the present API nomograph for obtaining TVP from RVP.

The method development and equipment costs would be relatively low using this approach if existing data were to be used to construct a new TVP-RVP nomograph for heavy crude oil as the actual test procedures would not be changed. The limitations on sampling and handling heavy crude oils would remain.

2. Direct Measurement of True Vapor Pressure

Essentially no support was found for pursuing this approach. The method requires use of an air-free sample and a V/L ratio approaching zero. There is no standardized method for the measurement of true vapor pressure. On a theoretical basis, the method is very sensitive to methane and other light ends content of the stock being measured. Thus the sampling procedure would be even more critical than with the RVP method. Methods development cost would be rather high. Equipment costs may not be too high as no compositional data are specifically required. Laboratory costs may be high depending upon the care needed to obtain accurate and repeatable results.

3. Modified RVP Method (Santa Barbara Approach)

This method involves collecting the crude oil sample directly in the liquid container portion of the vapor pressure apparatus thus eliminating the transfer of sample after collection. It is run at stock storage temperature. This eliminates the problem implicit in ASTM D323-72 requiring cooling of sample to 32-40°F before transferring it from the sample container to the test apparatus liquid chamber. Thus, samples which cannot be poured at 32 to 40°F still can be run using the modified procedure. The complete procedure as supplied by the Santa Barbara County Air Pollution Control District is given in Appendix A of this report.

The modified RVP procedure has several advantages and disadvantages. Already mentioned is elimination of the sample transfer problem. However, this also eliminates the opportunity for partial air saturation of the sample. Therefore, the developmental work should include parallel determinations by the standard RVP procedure where possible to determine the influence of this change. In general, a lesser degree of sample air saturation would tend to lower the vapor pressure measured as some of the air in the air chamber would dissolve in the sample during conduct of the test.

Perhaps a more serious problem with this method is that related to air saturation of the sample. In the Reid method, there is provision for partial air saturation by means of shaking the sample container after cooling to 32 to 40°F. The sample container has an air space so the shaking action results in the partial saturation. In the Santa Barbara modification, the sample is collected in the analysis container and there is no means for conducting the air saturation step. Thus, upon connecting the air chamber to the sample container and heating to the analysis temperature, there is some possibility that additional air will be dissolved depending upon the degree of saturation of air in the crude oil at time of sample collection.

The error will be in a negative direction, but is not determinate. The modified method is designed to conduct the vapor pressure measurement at stock storage temperature. This eliminates the need for a correlation nomograph. On the other hand, individual determinations would be necessary for each temperature of interest.

Because the test proposed uses the same V/L ratio as the standard RVP method, the influence of light ends should not change greatly.

Fairly extensive field testing of this method would be required in the developmental stage. Equipment and laboratory costs should not differ greatly from the standard RVP method.

4. Vapor Composition Method

The general principal of this approach involves analysis of the headspace vapor in equilibrium with a liquid crude oil sample. The vapor pressure is assumed to be a product of the mol fraction of hydrocarbon vapor in the headspace times the absolute pressure. The method eliminates interference from water vapor and dissolved air. It does assume that an accurate measurement of the hydrocarbon present in the vapor space can be made, however. Normally this would be done by an appropriate gas chromatographic method.

Two methods involving this approach have been reviewed. One, from the California Air Resources Board, involves collection of a sample in a 300 cc cylinder, which prior to the vapor analysis step, is connected to a 30 cc evacuated chamber. The two are connected, creating a vapor space. After the connected vessels are held for 30 minutes at the analysis temperature, the vapor space is opened to atmosphere long enough for the vapor space pressure to rise to one atmosphere. Aliquot samples of the vapor-air mixture are thus withdrawn and analyzed by gas chromatograph. As can be seen, the

determination is made at a V/L ratio or 1/11 (30/330). A preliminary draft of this method is given in Appendix B. A second vapor composition method was submitted by Chevron Research Company. In this method a sample is collected by the water displacement method. Prior to sample collection the sample container is filled with water on the clean side of a flexible impervious membrane. The membrane is free to move so as to allow the entire volume of a rigid container to be filled. The sample is collected from a sampling tap on the sampling side of the container by displacing an exact volume of water into another container. This latter container is removed and the remaining water drains from the clean side of the membrane. At the same time the sample side of the container is pressurized with nitrogen. The container is then allowed to come to equilibrium at the desired analysis temperature.

Aliquot vapor-N_2 samples are then withdrawn for gas chromatograph analysis similar to the CARB approach. The method as submitted suggests a V/L ratio of 4/1. This mthod is included as Appendix C to this report.

Both of the vapor composition methods can provide results on a methane or methane + ethane-free basis; thus reducing the variable influence of non-reactive hydrocarbons on the vapor pressure. Both specific methods require a reliable gas chromatographic analysis step. The Chevron method, as submitted, is restricted to tap or line sampling.

The vapor composition methods would require rather extensive field and laboratory testing and would increase the cost of analysis because of the gas chromatograph step. Not all control agencies have access to such equipment in-house.

5. Evaporation Method

This method involves determination of the loss of mass over time of a sample held at a specified temperature. While it is

one approach at obtaining a direct measure of evaporation loss instead of one which uses a measure of the potential to evaporate (such as vapor pressure), substantial questions on design of the test conditions would have to be answered. These include method of achieving test temperature -- oven or bath, rate of air or nitrogen sweep across the liquid surface, surface to volume ratio of the evaporation container, length of test, and quantity of stock to be used in the test. Finally, some new criterion would have to be developed as to whether the stock tested would have to be stored in a controlled tank. The method might be more applicable to open storage or waste ponds than it would be to tanked storage. This method is described more fully in Appendix D. This method would require extensive developmental work, but would be low in equipment and laboratory costs.

The various measures of heavy crude oil volatility are summarized in Table 1 against the evaluation criteria specified for use in this study.

TABLE 1. MEASURES OF HEAVY CRUDE OIL VOLATILITY VERSUS EVALUATION CRITERIA

Methods	Evaluation Criteria: Cost of Method Development	Equipment and Lab Costs	Repeatability	Sources of Error	Conformity to API Nomograph
Extrapolate API Nomograph	Gather additional data which in part should be available.	No new costs.	Unknown to fair. Takes into account gravity.	Sampling - Loss of C_1 and C_2 in various amounts. Needs to be run correctly regarding H_2O and barometric pressure.	Could be good depending on sampling and comparability of new curve data.
Equilibrium (True) Vapor Pressure Method	Extensive field testing.	Modest.	Poor	Extremely sensitive to C_1 and C_2 loss.	Not good. C_1 and C_2 effect.
Modified RVP	Extensive field testing.	Modest.	Fair to good.	No opportunity for air saturation.	Should measure all C_1 and C_2 to get good correlation.
Vapor Composition Method	Extensive lab and field testing.	Fairly high - need G.C.	Possibly good.	Accuracy of G.C. analysis possible problem. Eliminates water and diss. air problem.	Probably not good because of unknown influence of C_1 and C_2 in API method.
Evaporation Method	Extensive lab and field testing. Also need to correlate with loss tests.	Modest if lab has balance and oven.	Poor	Conditions have to be carefully controlled. How to relate to losses.	Unknown to poor.

SECTION 5

CONCLUSIONS AND RECOMMENDATIONS

The results of our analysis of methods potentially useful for measuring the volatilities of heavy crude oil were reviewed to determine whether any single candidate method clearly outranked the others according to the rating criteria. This appeared to us not to be the case. We did eliminate two methods from further consideration. These were (1) the Equilibrium (True) Vapor Pressure Method, and (2) the Evaporation Method. The former was eliminated because of the perceived experimental difficulties, the extreme sensitivity to methane and ethane content, and the lack of any information suggesting that any of the problems with use of the current RVP method would be eliminated. The evaporation approach was eliminated because of the significant departure from current measures of volatility, particularly as related to predictive loss equations for tank storage of petroleum. The method does appear to be useful for sumps, pits and open oil tanks.

Further review of the analysis results suggested that several rather specific objectives should be achieved by any new method. These include:

(1) It should permit sampling and testing of higher viscosity crude oils.

(2) It should permit determination of a volatility parameter for storage temperature above 140°F and RVPs (as currently measured) below 2 psi.

(3) It should reduce substantially the variable influence of methane and ethane present in the crude oil.

(4) It should be rugged enough to be conducive to good repeatability.

(5) The equipment and laboratory costs should permit reasonably widespread use.

Our recommendations were also influenced by the information that the American Petroleum Institute Committee on Evaporation Loss in the

process of collecting currently available data relating RVP to TVP measurements. This could result in the publication of a revised RVP versus TVP nomograph utilizing a broader data base and which includes an alignment grid for crude oils of different API gravities. The current nomograph has a single correlation line representing all crude oils instead of a grid. Therefore, we do not recommend at this time any supplemental work to extrapolate the current API nomograph.

The two remaining methods in consideration are the Santa Barbara modification of the RVP method and the vapor composition method. While the modified RVP method does address the sampling and transfer problems with the current RVP method, it does not solve the problem caused by light ends and possibly exacerbates the air saturation effect. Therefore, we recommend selection of the vapor composition method as a subject for a methods development and evaluation program. Where restrictions on ASTM D323-72 for determination of RVP permit, intercomparisons between vapor composition results and RVP should be included in the research program.

We suggest that the following parameters be considered in any experimental design developed for a reasearch program:

- Crude type - covering a range of API gravities, viscosities, light ends content
- Sampling procedure - dip, water displacement, with and without transfer from sample container to analysis container
- Vapor to liquid ratio
- Temperature of analysis
- Specific analytical procedure - standard RVP, vapor composition, etc.
- Number of replicates

Because the light ends content of some crudes can change quite rapidly after withdrawal from a well in a production field, it will be

important to consider exact location of sample withdrawal. It may be desirable to carry out analyses of liquid composition in at least a portion of the crude samples.

We have prepared a preliminary estimate of the level of effort to conduct the research and development effort suggested. Our estimate is based upon examination of ten crude oil types, two methods of analysis, three V/L ratios, two temperatures, and three replications. This results in about 450 samples. For this program we estimate an overall technical effort in the range of 2,000 to 3,000 hours. Other direct charges would include equipment, travel, per diem, expendable supplies, computer costs, communication, and reproduction.

A preliminary cost estimate has also been made for equipment needed by users to conduct both the standard RVP method and the vapor composition method. This estimate is given in Appendix E.

For sumps, ponds, and open tanks, we suggest further development of the procedure described in Appendix D.

REFERENCES

1. "Evaporation Loss from External Floating-Roof Tanks," API Publication 2517, Second Edition, February 1980, American Petroleum Institute, Washington, D.C.

2. "Hydrocarbon Emissions During Maring Loading of Crude Oils," Chevron Research Corporation for Western Oil and Gas Association, August 1977.

3. "Hydrocarbon Emissions from Fixed-Roof Petroleum Tanks," for Western Oil and Gas Association by Engineering-Science, Inc., July 1977.

4. "Evaporation Loss in the Petroleum Industry - Causes and Control," API Publication No. 2513, reaffirmed 1973, American Petroleum Institute, Washington, D.C.

NON-REFERENCED CONTACTS

1. Richard Burr, U.S. Environmental Protection Agency, OAQPS, RTP, NC.

2. Harry Metzger, California Air Resources Board, Sacramento, CA.

3. Abe Moore, South Coast Air Quality Management District, El Monte, CA.

4. T. H. Gouw, Chevron Research Co., Richmond, CA.

5. Sam Fett, Union Oil Research Co., Brea, CA.

6. John English, Santa Barbara County Air Pollution Control District, Santa Barbara, CA.

7. Robert A. Farnham, Chevron Research Co., Richmond, CA.

APPENDIX A

SANTA BARBARA MODIFIED RVP APPROACH

SANTA BARBARA VAPOR PRESSURE FOR CRUDE OILS

SCOPE

This method is designed to determine a vapor pressure of crude oils at the temperature at which they are being stored.

EQUIPMENT

Equipment and apparatus are those used in the Reid Method (ASTM D323) with the modification shown in Figure 1.

PROCEDURE

Sampling:

1. Evacuate a clean, dry liquid chamber by suitable means to 1 mm Hg or less absolute and close the valves.
2. Submerge the evacuated liquid chamber 3' to 5' below the surface of the crude oil in the storage tank and open the top valve to allow the crude to enter and fill the chamber. Reclose the chamber while submerged and remove from the tank. Clean the crude from the outside of the liquid chamber.
3. Place the sealed liquid chamber in an ice water bath or crushed ice to transport it to wherever the test is to be conducted.
4. Determine the temperature of the crude in the storage tank.

MEASUREMENT OF THE VAPOR PRESSURE

1. Prepare the air chamber as outlined in the modified ASTM procedure Section 6.3 attached. The test is run at the nearest 5°F above the temperature of the tank sampled.

2. Quickly assemble the liquid and air chambers and return to the bath at the test temperature. Do not open the interconnecting valve until the sample is at the test temperature (about 20 minutes). Agitate the sample as described in the ASTM procedure, following that procedure from Section 7.4 to completion. Record the gauge reading as the vapor pressure and indicate the temperature at which the measurement was made.

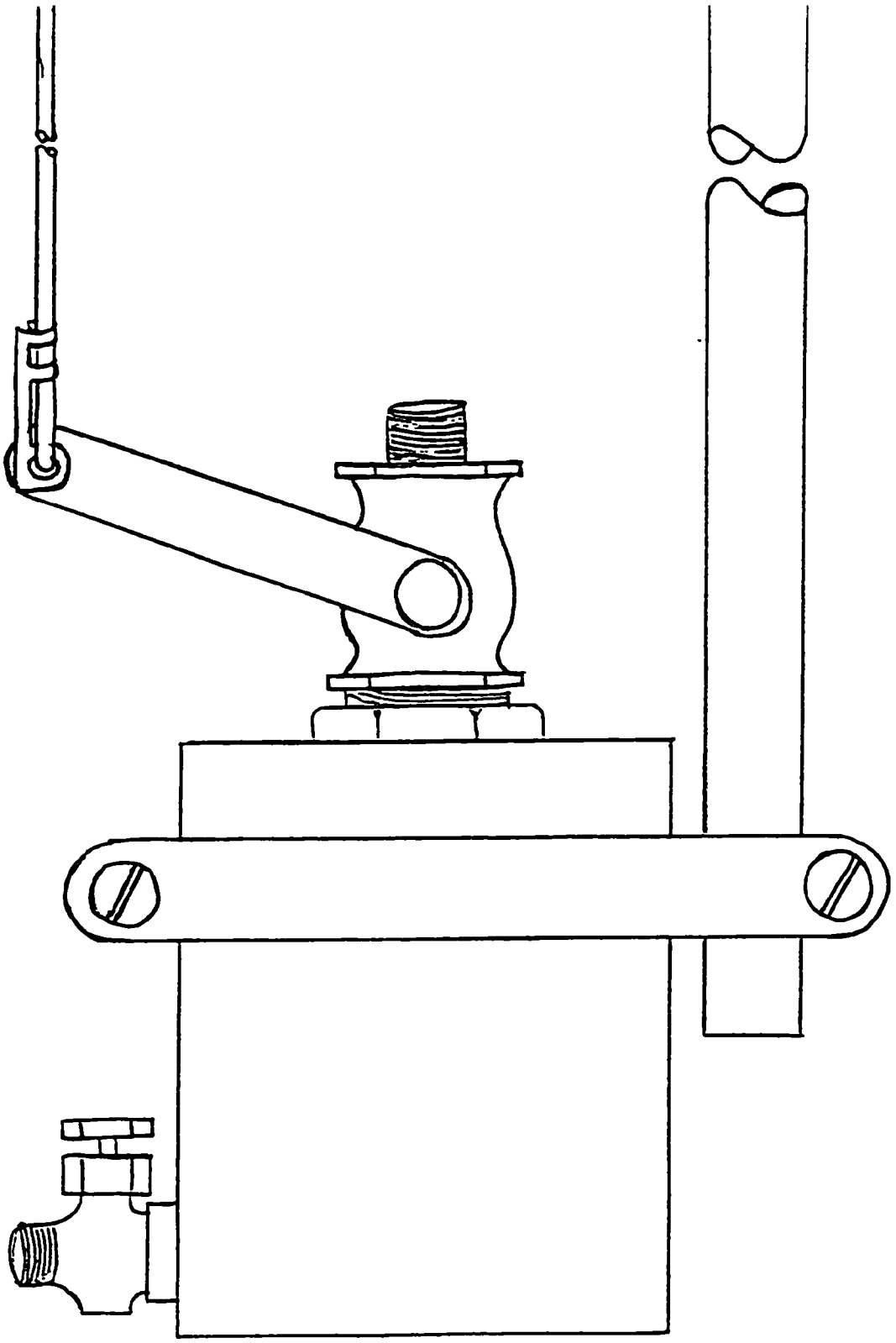

Figure 1

Designation: D 323 – 72

American National Standard Z11.44-1973
Approved June 4, 1973
By American National Standards Institute

Standard Method of Test for VAPOR PRESSURE OF PETROLEUM PRODUCTS (REID METHOD)[1]

This Standard is issued under the fixed designation D 323, the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 This method covers the determination of the absolute vapor pressure (Note 1) of volatile crude oil and volatile nonviscous petroleum products, except liquefied petroleum gases (Note 2).

NOTE 1—Because the external atmospheric pressure is counteracted by the atmospheric pressure initially present in the air chamber, the "Reid vapor pressure" is an absolute pressure at 100 F in pounds per square inch. The "Reid Vapor Pressure" differs from the true vapor pressure of the sample due to some small sample vaporization and the presence of water vapor and air in the confined space.

NOTE 2—For determination of the vapor pressure of liquefied petroleum gases reference should be made to Method D 1267.

NOTE 3—The values stated in U.S. customary units are to be regarded as the standard.

2. Applicable Documents

2.1 *ASTM Standards:*

D 270 Sampling Petroleum and Petroleum Products[2]

D 1267 Test for Vapor Pressure of Liquefied Petroleum (LP) Gases (LP Gas Method)[3]

E 1 Specification for ASTM Thermometers[4]

3. Summary of Method

3.1 The gasoline chamber of the vapor pressure apparatus is filled with the chilled sample and connected to the air chamber at 100 F or other temperature. The apparatus is immersed in a constant-temperature bath (100 ± 0.2 F) and is shaken periodically until equilibrium is reached. The "manometer reading" corresponding to the pressure read on the gage attached to the apparatus, suitably corrected (Table 1) if the air chamber was initially at a temperature other than 100 F, is the *Reid vapor pressure*.

3.2 This method provides for prior air saturation of products with Reid vapor pressure below 26 lb (Sections 1 to 9, and 17), for air saturation for products above 26 lb (Sections 10 to 15, and 17) and for narrower tolerances and features for the measurement of the vapor pressure of aviation gasolines (Sections 16 and 17).

4. Apparatus

4.1 The construction of the required apparatus is described in the Appendix. For samples having vapor pressures below 26 lb, use the gasoline chamber with one opening (A1.1.2) and for samples having vapor pressures above 26 lb, use the gasoline chamber with two openings (A1.1.3).

5. Handling of Samples

5.1 The general provisions in 5.2 and 5.6 shall apply to all samples for vapor pressure determinations, except as specifically excluded for samples having vapor pressures above 26 lb (see Section 12). The extreme sensitivity of vapor pressure measurements to losses through evaporation and to slight changes in composition is such as to require the utmost precaution and the most meticulous care in the handling of samples.

5.2 Sampling shall be done in accordance with the procedure for Reid vapor pressure as described in Method D 270.

5.3 *Sample Container Size*—The size of the sample container from which the vapor pressure sample is taken shall be not less than 1 qt nor more than 2 gal.

5.4 *Sample Handling Temperature*—In all cases the sample container and its contents shall be cooled to 32 to 40 F before the con-

[1] This method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants.

Current edition approved Aug. 29, 1972. Published October 1972. Originally published as D 323 – 30. Last previous edition D 323 – 58 (1968).

[2] *Annual Book of ASTM Standards*, Part 23.

[3] *Annual Book of ASTM Standards*, Parts 25 and 44.

tainer is opened

5.5 *Sample Transfer*—The Reid vapor pressure determination shall be the first test run on a sample. In the instances of transfer of liquids from larger sample containers or of withdrawal of samples for other tests, the transfer connection of Fig. 1 shall be used.

5.6 *Care of Samples*—Samples shall be put in a cool place as soon as possible after they have been obtained and held there until the test has been completed. Samples in leaky containers shall not be considered for test but shall be discarded and new samples obtained.

6. Preparation for Test

6.1 *Air Saturation of Sample in Sample Container*—With the sample at a temperature of 32 to 40 F, take the container from the water cooling bath, unseal it, and examine it for its liquid content, which shall be between 70 and 80 percent of the container capacity. After the correct liquid content has been assured, reseal the container, shake vigorously, and return it to the water cooling bath.

6.2 *Preparation of Gasoline Chamber*—Completely immerse the gasoline chamber and the sample transfer connection in the water cooling bath for a sufficient time to allow the chamber and connection to reach the bath temperature (32 to 40 F).

6.3 *Preparation of Air Chamber (Water Bath Procedure)*—After purging and rinsing the air chamber and pressure gage in accordance with 7.5, connect the gage to the air chamber. Immerse the air chamber to at least 1 in. above its top in the water bath maintained at 100 F, for not less than 10 min just before coupling it to the gasoline chamber. Do not remove the air chamber from the bath until the gasoline chamber has been filled with sample as described in 7.1.

6.4 *Preparation of Air Chamber (Ambient Temperature Procedure)*—As an alternative to 6.3, adjust the air chamber to ambient or other temperature which may be determined with an accuracy of at least 1 F in the following manner: After purging and rinsing the air chamber and pressure gage in accordance with 7.1, connect the gage to the air chamber. Insert the thermometer into the air chamber, supporting it by means of a loosely fitting (not airtight) stopper in the opening of the air chamber. Adjust the position of the thermometer so that it is aligned as closely as possible with the axis of the air chamber, and with the thermometer bulb located in the air chamber, about 9 in. from the opening. Leave the thermometer in position until the temperature reading has remained constant within 1 F for a period of 5 min or more just before coupling the air chamber to the gasoline chamber. At this time, record the thermometer reading as the "initial air temperature."

7. Procedure

7.1 *Sample Transfer*—With everything in readiness, remove the chilled sample container from the bath, uncap it, and insert the chilled transfer connection and air tube (see Fig. 1). Quickly empty the chilled gasoline chamber and place it over the sample delivery tube of the transfer connection. Invert the entire system rapidly so that the gasoline chamber is finally in an upright position with the delivery tube extending to within 1/4 in. of the bottom of the gasoline chamber. Fill the gasoline chamber to overflowing. Lightly tap the gasoline chamber against the workbench to ensure that the sample is free of air bubbles. If any sample is displaced, refill the chamber to overflowing.

7.2 *Assembly of Apparatus*—Without delay, and as quickly as possible, attach the air chamber to the gasoline chamber. Not more than 20 s shall be consumed in completing the assembly of the apparatus after filling the gasoline chamber, using the following sequence of operations.

7.2.1 Invert the gasoline chamber to fill connecting tube.

7.2.2 Read the initial air temperature of the air chamber (6.4), or remove the air chamber from the 100 F water bath (6.3).

7.2.3 Connect the air chamber to the gasoline chamber.

7.3 *Introduction of Apparatus into Bath*—Immerse the assembled apparatus in the bath, maintained at 100 F, in an inclined position so that the connection of the gasoline and air chambers is

with a suitable solvent and dry with air and heat as may be required. Care should be taken to be sure that the Bourdon tube of the pressure gauge is thoroughly clean and dry.

below the water level and may be observed closely for leaks. If no leaks are observed, immerse the apparatus to at least 1 in. above the top of the air chamber Observe the apparatus for leaks throughout the test. When at any time a leak is detected, discard the test

NOTE 4—Liquid leaks are more difficult to detect than vapor leaks, and because the much-used coupling device is normally in the liquid section of the apparatus, give it particular attention

7.4 *Measurement of Vapor Pressure*—After the assembled vapor pressure apparatus has been immersed in the bath for 5 min, tap the pressure gage lightly, and observe the reading. Withdraw the apparatus from the bath, invert it, shake it vigorously, and replace it in the bath in the shortest possible time to avoid cooling the apparatus. At intervals of not less than 2 min, repeat this agitation and gage observation at least five times, until the last two consecutive gage readings are constant, to ensure equilibrium. These operations normally require 20 to 30 min. Read the final gage pressure to the nearest 0.05 lb for gages with intermediate graduations of 0.1 psi and to the nearest 0.1 lb for gages with graduations of 0.2 to 0.5 psi, and record this value as the "uncorrected vapor pressure" of the sample under test. Immediately remove the pressure gage and check its reading against that of the manometer, recording the value found as the Reid vapor pressure (under the procedure of 6.3), or as the "manometer reading" to be used in the calculations of Section 9 (under the procedure of 6.4)

liquid

7.5 *Preparation of Apparatus for Next Test*—Disconnect the air chamber, ~~gasoline~~ chamber, and pressure gage [redacted] in the Bourdon tube by repeated centrifugal thrusts. This may be accomplished in the following manner: hold the gage between the palms of the hands with the right hand on the face side and the threaded connection of the gage forward. Extend the arms forward and upward at an angle of 45 deg with the coupling of the gage pointing in the same direction. Swing the arms downward through an arc of about 135 deg so that the centrifugal force aids gravity in removing the trapped liquid. Repeat this operation three times to expel all liquid. Purge the pressure gage by directing a small jet of air [redacted] its Bourdon tube for at least 5 min Thoroughly purge the air chamber of residual sample by filling the air chamber with warm water (about 100 F) and allowing it to drain (Note 6) Repeat this purging at least five times After thoroughly removing the previous sample from the gasoline chamber, immerse the chamber in the ice bath for the next test

NOTE 5—In the case of crude oil, the Bourdon tube must be washed with a volatile solvent after each test

NOTE 6—If the purging of the air chamber is done in a bath, be sure to avoid small and unnoticeable films of floating sample covering the bottom and top openings of the chamber as they pass through the surface of water

8. Precautions

8.1 Gross errors can be obtained in vapor pressure measurements if the prescribed procedure is not followed carefully. The following list emphasizes the importance of strict adherence to the precautions given in the procedure:

8.1.1 *Checking the Pressure Gage*—Check all gages against a manometer after each test in order to ensure higher precision of results (7.4). Read all gages while the gage is in a vertical position

8.1.2 *Air Saturation of Sample*—Open and close the sample container once after the contents have reached a temperature of 32 to 40 F. Shake the container vigorously to ensure equilibrium between the sample with the air in the container (6.1).

8.1.3 *Checking for Leaks*—Check all apparatus before and during each test for liquid and vapor leaks (A1.1.6 and Note 4).

8.1.4 *Sampling*—Because initial sampling and the handling of samples will greatly affect the test results, employ the utmost precaution and the most meticulous care to avoid losses through evaporation and slight changes in composition (see Sections 5 and 7.1). In no case shall any part of the Reid apparatus itself be used as the sample container previous to actually conducting the test.

8.1.5 *Purging the Apparatus*—Thoroughly purge the pressure gage, the gasoline chamber, and the air chamber to be sure that they are free of residual sample. (This is most conveniently done at the end of the previous test.) (See 7.5).

8.1.6 *Coupling the Apparatus*—Carefully

observe the requirements of 7.2

8.1.7 *Shaking the Apparatus*—Shake the apparatus "vigorously" as directed in 7.4 in order to ensure equilibrium

8.1.8 *Temperature Control*—Carefully control the temperature at the time of air saturation and the temperature of the 100 F bath (Appendix, A1.3 and A1.4, respectively). Be certain that the temperature of the air in the air chamber at the time of coupling with the liquid gasoline chamber (7.2) has remained constant within 1 F for a period of 5 min or more.

9. Calculation

9.1 *Change in Pressure of Water Vapor and Air*—For the ambient temperature procedure described in 6.4, calculate the "Reid vapor pressure" of the sample under test by applying to the "manometer reading" the correction given in Table 1 for the change in pressure of the water vapor and air in the chamber on heating from the "initial air temperature" to 100 F.

9.2 *Recording Results*—When [illegible], record the result observed in 7.4 as the "uncorrected vapor pressure" in pounds with reference to temperature of [illegible] procedure (6.3 and 9.1) was used, record the value resulting from the application of the correction from 9.1 as the "corrected vapor pressure" with reference to temperature of [illegible].

Modifications for Products Having Reid Vapor Pressures above 26 lb

10. General

10.1 With products having vapor pressures over 26 lb (Note 7), the procedure described in Sections 5 to 8 is hazardous and inaccurate. Consequently, the following sections define changes in apparatus and procedure for the determination of vapor pressures above 26 lb. Except as specifically stated, all the requirements of Sections 1 to 9 and Section 17 shall apply.

NOTE 7—When the question arises, the air saturation method shall be used to determine whether or not a product has a vapor pressure above 26 lb.

11. Apparatus

11.1 *Bomb*, as described in the Appendix using the gasoline chamber with two openings

11.2 *Pressure Gage Calibration*—A dead-weight tester (A1.7) may be used in place of the mercury manometer (A1.6) for checking gage readings above 26 lb. In 7.4, 8.1.1, and 9.1, and Table 1 where the words "manometer" and "manometer reading" appear, include as an alternate "dead-weight tester" and "calibrated gage reading," respectively

12. Handling of Samples

12.1 5.3, 5.4, and 5.5 shall not apply.

12.2 *Sample Container Size*—The size of the sample container from which the vapor pressure sample is taken shall not be less than 1 pt liquid capacity.

13. Preparation for Test

13.1 6.1 and 6.2 shall not apply.

13.2 Any safe method of displacement of the test sample from the sample container that assures filling the gasoline chamber with a chilled, unweathered sample may be employed. The following 13.3 to 13.5, together with Section 14, describe displacement by self-induced pressure.

13.3 Maintain the sample container at a temperature sufficiently high to maintain superatmospheric pressure but not substantially over 100 F.

13.4 Completely immerse the gasoline chamber, with both valves open, in the water cooling bath for a sufficient length of time to allow it to reach the bath temperature (32 to 40 F).

13.5 Connect a suitable ice-cooled coil to the outlet valve of the sample container.

NOTE 8—A suitable ice-cooled coil can be prepared by immersing a spiral of approximately 5 ft of $^1/_4$-in. copper tubing in a bucket of ice water

14. Procedure

14.1 7.1 and 7.2 shall not apply.

14.2 Connect the $^1/_4$-in. valve of the chilled gasoline chamber to the ice-cooled coil. With the $^1/_2$-in. valve of the gasoline chamber closed, open the outlet valve of the sample container and the $^1/_4$-in. valve of the gasoline chamber. Open the gasoline chamber $^1/_2$-in. valve slightly-and-allow the gasoline chamber to fill slowly. Allow the sample to overflow until the overflow volume is 20 ml or more. Control this operation so that no appreciable

drop in pressure occurs at the gasoline chamber $^1/_4$-in. valve. In the order named, close the gasoline chamber $^1/_2$-in. and $^1/_4$-in. valves; and then close all other valves in the sample system. Disconnect the gasoline chamber and the cooling coil. (Caution: Safe means for disposal of liquid and vapor escaping during this whole operation must be provided. To avoid rupture because of the liquid-full condition of the gasoline chamber, the gasoline chamber must be quickly attached to the air chamber and the $^1/_4$-in. valve opened.)

14.3 Immediately attach the gasoline chamber to the air chamber and open the gasoline chamber $^1/_2$-in. valve. Not more than 25 s shall be consumed in completing the assembly of the apparatus after filling the gasoline chamber, using the following sequence of operations: (*1*) read the initial air temperature or remove the air chamber from the water bath, (*2*) connect the air chamber to the gasoline chamber, and (*3*) open the gasoline chamber $^1/_2$-in. valve.

14.4 If a dead-weight tester is used instead of the mercury manometer (11.2), apply the calibration factor in pounds per square inch established for the pressure gage at or near the "uncorrected vapor pressure" to the "uncorrected vapor pressure," recording the value found as the "calibrated gage reading" to be used in the calculations of Section 9 and Table 1 in place of the "manometer reading."

15. Precautions

15.1 The precaution 8.1.3 shall not apply.

Modifications for Aviation Gasoline of About 7 lb Vapor Pressure

16. General

16.1 The following paragraphs define changes in apparatus and procedure for the determination of the vapor pressure of aviation gasoline. Except as specifically stated herein, all the requirements set forth in Sections 1 to 9 and 17 shall apply.

16.1.1 *Ratio of Air and Gasoline Chambers*—The ratio of the volume of the air chamber to the volume of the gasoline chamber shall be between the limits of 3.95 and 4.05 (see Note A1 in the Appendix).

16.1.2 *Water Cooling Bath*—The water cooling bath shall be held at a temperature of 32 to 34 F (See A1.3).

16.1.3 *Checking the Pressure Gage*—The gage shall be checked at 7 lb against a mercury column before each vapor pressure measurement to ensure that it conforms to the requirements of Section A1.2. This preliminary check shall be made in addition to the final gage comparison specified in 7.4.

16.1.4 *Air Chamber Temperature*—The provisions of 6.3 shall be followed; the provisions of 6.4 shall not apply.

17. Precision

17.1 The following criteria should be used for judging the acceptability of results (95 percent confidence):

17.1.1 *Repeatability*—Duplicate results by the same operator should be considered suspect if they differ by more than the following amounts:

Range	Repeatability (Same Operator and Apparatus)
0 to 5 lb	0.1
5 to 16 lb (except aviation gasoline)	0.2
16 to 26 lb	0.3
Above 26 lb	0.4
Aviation gasoline (approximately 7 lb)	0.1

17.1.2 *Reproducibility*—The results submitted by each of two laboratories should be considered suspect if they differ by more than the following amounts:

Range	Reproducibility (Different Operator and Apparatus)
0 to 5 lb	0.35
5 to 16 lb (except aviation gasoline)	0.3
16 to 26 lb	0.4
Above 26 lb	0.7
Aviation gasoline (approximately 7 lb)	0.15

TABLE 1 Corrections to be Subtracted from "Manometer Readings" for Calculating Reid Vapor Pressure

Initial Air Temperature,[a] deg F	Barometric Pressure,[a] mm Hg		
	760	700	600
32	2.90	2.70	2.45
40	2.60	2.45	2.20
50	2.20	2.10	1.90
60	1.80	1.70	1.55
70	1.40	1.30	1.20
80	0.95	0.90	0.85
90	0.50	0.50	0.45
100	0.00	0.00	0.00
110	−0.55	−0.55	−0.50

[a] For other temperatures and pressures, the corrections may be calculated by means of the following equation:

Correction = $|(P - P_t)(t - 100)/460 + t| - .(P_{100} - P_t)$

where:

t = air chamber temperature at beginning of test, deg F.

P = barometric pressure, psi, at time of test (if a barometer is not available, the normal barometric pressure may be used),

P_t = vapor pressure of water, psia, at t deg F, and

P_{100} = vapor pressure of water, psia, at 100 F = 0.95.

Calculated corrections are to be rounded off to the nearest 0.05 psi.

Example—The pressure gage gives an "uncorrected vapor pressure" reading of 11.6 psi. When the gage is compared to a mercury column, a "manometer reading" of 11.5 psi is obtained. For an "initial air temperature" of 80 F and atmospheric pressure of 700 mm Hg, the correction shown in Table 1 is 0.90 psi. Because the "initial air temperature" is below 100 F, this correction of 0.90 psi is subtracted from the "manometer reading" of 11.5 psi giving, a "Reid vapor pressure" of 10.60 psi.

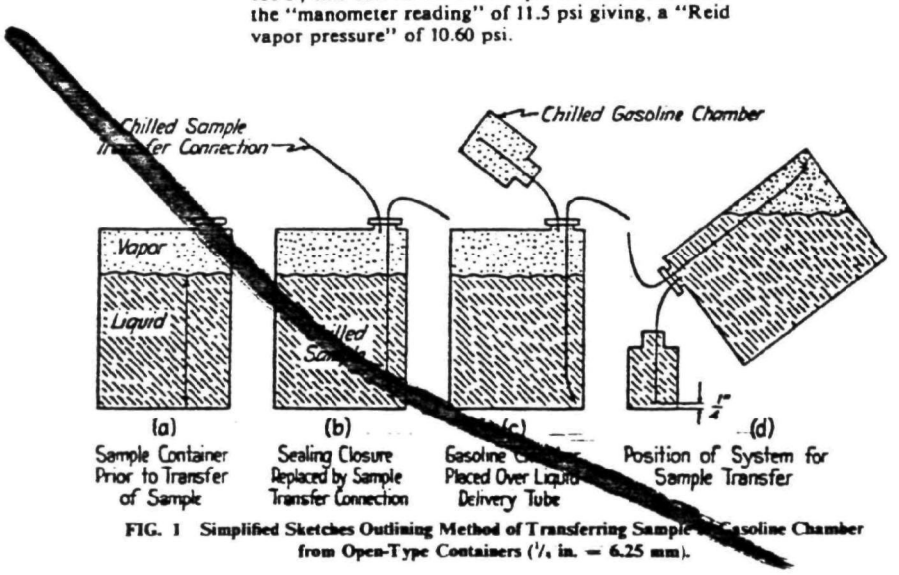

FIG. 1 Simplified Sketches Outlining Method of Transferring Sample to Gasoline Chamber from Open-Type Containers (1/4 in. = 6.25 mm).

APPENDIX

A1. Apparatus for Reid Vapor Pressure Test

A1.1 *Reid Vapor Pressure Bomb*, consisting of two chambers—an air chamber (upper section) and a gasoline chamber (lower section)—shall conform to the following requirements

NOTE A1: Caution—*To maintain the correct volume ratio between the air chamber and the gasoline chamber, the units shall not be interchanged without recalibrating to ascertain that the volume ratio is within satisfactory limits*

A1.1.1 *Air Chamber*—The upper section or air chamber, as shown in FIG. A1, shall be a cylindrical vessel 2 ± $^1/_8$ in. in diameter and 10 ± $^1/_8$ in. in length, inside dimensions, with the inner surfaces of the ends slightly sloped to provide complete drainage from either end when held in a vertical position On one end of the air chamber, a suitable gage coupling with an internal diameter not less than $^5/_{16}$ in. shall be provided to receive the $^1/_4$-in. gage connection. In the other end of the air chamber an opening approximately $^1/_2$ in. in diameter shall be provided for coupling with the gasoline chamber. Care shall be taken that the connections to the end openings do not prevent the chamber from draining completely.

A1.1.2 *Gasoline Chamber (One-Opening)*—The lower section or gasoline chamber, as shown in Fig. A1, shall be a cylindrical vessel of the same inside diameter as the air chamber and of such volume that the ratio of the volume of the air chamber to the volume of the gasoline chamber shall be between the limits of 3.8 and 4.2 (see Note A2). In one end of the gasoline chamber an opening approximately $^1/_2$ in. in diameter shall be provided for coupling with the air chamber. The inner surface of the end containing the coupling member shall be sloped to provide complete drainage when inverted. The other end of the gasoline chamber shall be completely closed.

NOTE A2—The ratio for units to be used for aviation gasoline testing shall be between 3.95 to 4.05.

A1.1.3 *Gasoline Chamber (Two-Opening)*—For sampling from closed vessels, the lower section or gasoline chamber, as shown in Fig. A1 shall be essentially the same as the [redacted] chamber described in A1.1.2, except that a $^1/_4$-in. valve shall be attached near the bottom of the [redacted] chamber and a $^1/_2$-in. straight-through, full-opening valve shall be introduced in the coupling between the chambers. The volume of the [redacted] chamber, including only the capacity enclosed by the valves, shall fulfill the volume ratio requirements as set forth in A1.1.2.
ments as set forth in A1.1.2.

NOTE A3—In determining capacities for the two-opening [redacted] chamber (Fig. A1), the capacity of the [redacted] chamber shall be considered as that below the $^1/_2$-in. valve closure. The volume above the $^1/_4$-in. valve closure including the portion of the coupling permanently attached to the gasoline chamber shall be considered as a part of the air chamber capacity

A1.1.4 *Method of Coupling Air and [redacted] Chambers*—Any method of coupling the air and [redacted] chambers may be employed, provided that no [redacted] is lost during the coupling operation, that no compression effect is caused by the act of coupling, and that the assembly is free from leaks under the conditions of the tests. To avoid displacement of [redacted] during assembly it is desirable that the male fitting of a suitable coupling be on the [redacted] chamber. To avoid compression of air during the assembly of a suitable screw coupling, a vent hole may be used to ensure atmospheric pressure in the air chamber at the instant of sealing

A1.1.5 *Volumetric Capacity of Air and [redacted] Chambers*—In order to ascertain if the volume ratio of the chambers is between the specified limits of 3.8 to 4.2 (see Note A2), measure a quantity of water greater than will be needed to fill the [redacted] and air chambers. The [redacted] chamber shall be completely filled with water, and the difference between the original volume and the remaining volume is the volume of the [redacted] chamber. Then after connecting the [redacted] and air chambers, the air chamber shall be filled to the seat of the gage connection with more of the measured water, and the difference in volumes shall be the volume of the air chamber

A1.1.6 *Checking for Freedom from Leaks*—Before placing new apparatus in service and as often as necessary thereafter, the assembled vapor pressure apparatus shall be checked for freedom from leaks by filling with air to 100-psi gage pressure and completely immersing in a water bath. Only apparatus which stands this test without leaking shall be used.

A1.2 *Pressure Gage*—The pressure gage shall be a Bourdon-type spring gage of test gage quality 4 $^1/_2$ to 5 $^1/_2$ in in diameter provided with a nominal $^1/_4$-in. male thread connection with a passageway not less than $^5/_{16}$ in. in diameter from the Bourdon tube to the atmosphere. The range and graduations of the pressure gage used shall be governed by the

Gage to be Used

Reid Vapor Pressure, lb	Scale Range, psi	Maximum Numbered Intervals, psi	Maximum Intermediate Graduations, psi
4 and under	0 to 5	1	0.1
3 to 12	0 to 15	3	0.1
10 to 26	0 to 30	5	0.2
10 to 36	0 to 45	5	0.2
30 to 55	0 to 60	10	0.25
50 and higher	0 to 100	10	0.5

vapor pressure of the sample being tested, as follows:

Only accurate gages shall be continued in use. When the gage reading differs from the manometer (or dead-weight tester when testing gages above 26 lb) reading by more than 1 percent of the scale range of the gage, the gage shall be considered inaccurate. For example, the calibration correction shall not be greater than 0.15 psi for a 0 to 15-psi gage or 0.3 psi for a 0 to 30-psi gage.

NOTE A4—Gages $3\frac{1}{2}$ in. in diameter may be used in the 0 to 5 lb range.[3]

A1.3 *Water Cooling Bath*—A water cooling bath shall be provided of such dimensions that the sample containers and [illegible] chambers may be completely immersed. Means for maintaining the bath at a temperature of 32 to 40 F shall be provided.

NOTE A5—Solid carbon dioxide shall not be used to cool samples in storage or in the preparation of the air saturation step. Carbon dioxide is appreciably soluble in gasoline, and its use has been found to be the cause of erroneous vapor pressure data.

A1.4 *Water Bath*—The water bath shall be of such dimensions that the vapor pressure apparatus may be immersed to at least 1 in. above the top of the air chamber. Means for maintaining the bath at a constant temperature of 100 ± 0.2 F shall be provided. In order to check this temperature, the bath thermometer shall be immersed to the 98 F mark throughout the vapor pressure determination.

A1.5 *Thermometers:*

A1.5.1 *For 100 F Air Chamber Procedure*—An ASTM Reid Vapor Pressure Thermometer No. 18F having a range from 94 to 108 F and conforming to the requirements in Specification E 1.

A1.5.2 *For Water Bath*—Use the ASTM Thermometer 18F described in A1.5.1.

A1.5.3 *For Air Chamber*—When the ambient temperature procedure is employed, a thermometer conforming to the following requirements shall be used: Length, approximately 12 in.; range, −40 or −30 F to +120 or +130 F; graduated in 1 F divisions; total immersion; scale error not greater than 1 F.

A1.6 *Mercury Manometer*—A mercury manometer, having a range suitable for checking the pressure gage employed shall be used. The manometer scale may be graduated in steps of 1 mm, 0.1 in., or 0.1 psi.

A1.7 *Dead-Weight Tester*—A dead-weight tester may be used in place of the mercury manometer (A1.6) for checking gage readings above 26 lb.

[3] Suitable gages are available from the Fisher Scientific Co. (Special Order), Pittsburgh, Pa. and U. S. Gauge Co. (Catalog No. 510SP), Sellersville, Pa.

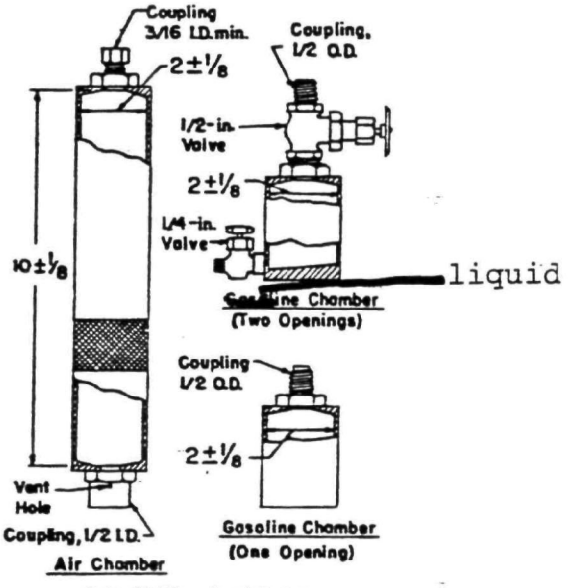

FIG. A1 Vapor Pressure Bomb.

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APPENDIX B

CALIFORNIA AIR RESOURCES BOARD
VAPOR COMPOSITION METHOD

Determination of Crude Oil Vapor Pressure
by Gas Chromatographic Vapor Analysis
(Draft Proposed Method)

SCOPE

This method is proposed to determine the approximate true vapor pressure (bubble point pressure), exclusive of the partial pressure of methane, for any crude oil at temperatures high enough for the oil to flow. The practicality and validity of the method for crude oil will be demonstrated in the laboratory. If subsequent testing of the method with other liquids is successful, the method's scope may be expanded. The method will be applicable only if the total vapor pressure, including methane, is less than 14.7 psia.

SUMMARY OF METHOD

Oil will be collected, by methods described elsewhere, in a 300 cc cylinder equipped with leak-tight valves at both ends and a rubber septum at one end. The entire volume of the cylinder will be full. The sample will be kept on ice pending analysis.

In the laboratory, an empty chamber of exactly 30 cc volume will be attached to the lower sample cylinder valve and evacuated. The cylinder valve will then be opened, creating a vapor space in the sample cylinder. The assembly, with the 30 cc chamber at the bottom, will be placed in a temperature bath until it has reached the desired analysis temperature throughout. Aliquots of equilibrium vapors will then be withdrawn through the septum at the upper cylinder valve with a syringe which is at the test temperature. The aliquots will be analyzed by gas chromatography

for the mass concentrations of hydrocarbons of each carbon number. The total non-methane vapor pressure will be calculated according to the perfect gas relationship from the sum of each mass concentration divided by the appropriate molecular weight.

EQUIPMENT

1. 300 cc stainless steel sampling cylinder equipped with vacuum-tight valves at each end and with a rubber sampling septum. See Figure 1. The total volume between the two valve closures shall be between 295 and 305 cc.
2. Vacuum chamber with two openings, one fitted with a vacuum tight valve, the other with a connector compatible with the lower sample cylinder valve. The volume of the chamber between the valve closure and the opening of the connector (points 1 and 2 in Figure 1) shall be 30.0 cc.
3. Vacuum pump capable of achieving 1.0 mm Hg.
4. Temperature bath capable of maintaining within 0.3°F of the desired temperature.
5. Gas chromatograph meeting the following specifications: (to be recommended by AIHL).
6. (Chromatographic column to be recommended by AIHL).
7. Syringe for chromatograph sample injection.

SAMPLING PROCEDURE

Samples will be collected in a 300 cc sample cylinder according to methods approved by the Air Resources Board. (A draft method is enclosed.) The sample cylinder will be completely full. The sample will be kept in ice until the headspace analysis is performed.

LABORATORY PROCEDURE

A. Gas Chromatograph Preparation (to be recommended by AIHL).

B. Sample Preparation

1. Clean the outlet of valve B (Figure 1).
2. Attach the 30.0 cc vacuum chamber to valve B and evacuate it to 1.0 mm Hg or less. Close valve D and verify that the chamber is vacuum-tight.
3. Close valve C, disconnect it from the vacuum line and place a rubber stopper over the valve outlet to prevent any leak through the valve.
4. Open valve B and immerse the entire assembly, with the 30 cc chamber down, in the temperature bath. Also immerse the syringe, enclosed to prevent contact with the bath fluid. Agitate the cylinder at five minute intervals.
5. After 30 minutes, open slightly valve A to allow the total pressure to rise to one atmosphere. Close the valve.
6. Insert the sample syringe, with the plunger slightly out, through the septum and depress the plunger completely (to eject any oil which enters the syringe needle during insertion).
7. Withdraw the desired aliquot volume and inject the aliquot into the chromatograph. Steps 6 and 7 should be done quickly to prevent cooling of the aliquot.
8. At ten minute intervals, withdraw and inject two additional aliquots per steps 5-7.

CALCULATIONS

1. Determine the total mass in the aliquot of each group of compounds with the same carbon number.

2. Calculate the total vapor pressure in the aliquot as:

$$P = \frac{RT}{V} \sum \frac{M_i}{MW_i}$$

Where:

R = gas constant

V = aliquot volume

T = test temperature

M_i = mass of compounds with carbon number i; all measurable hydrocarbons except methane

MW_i = molecular weight of carbon number i compounds

PRELIMINARY

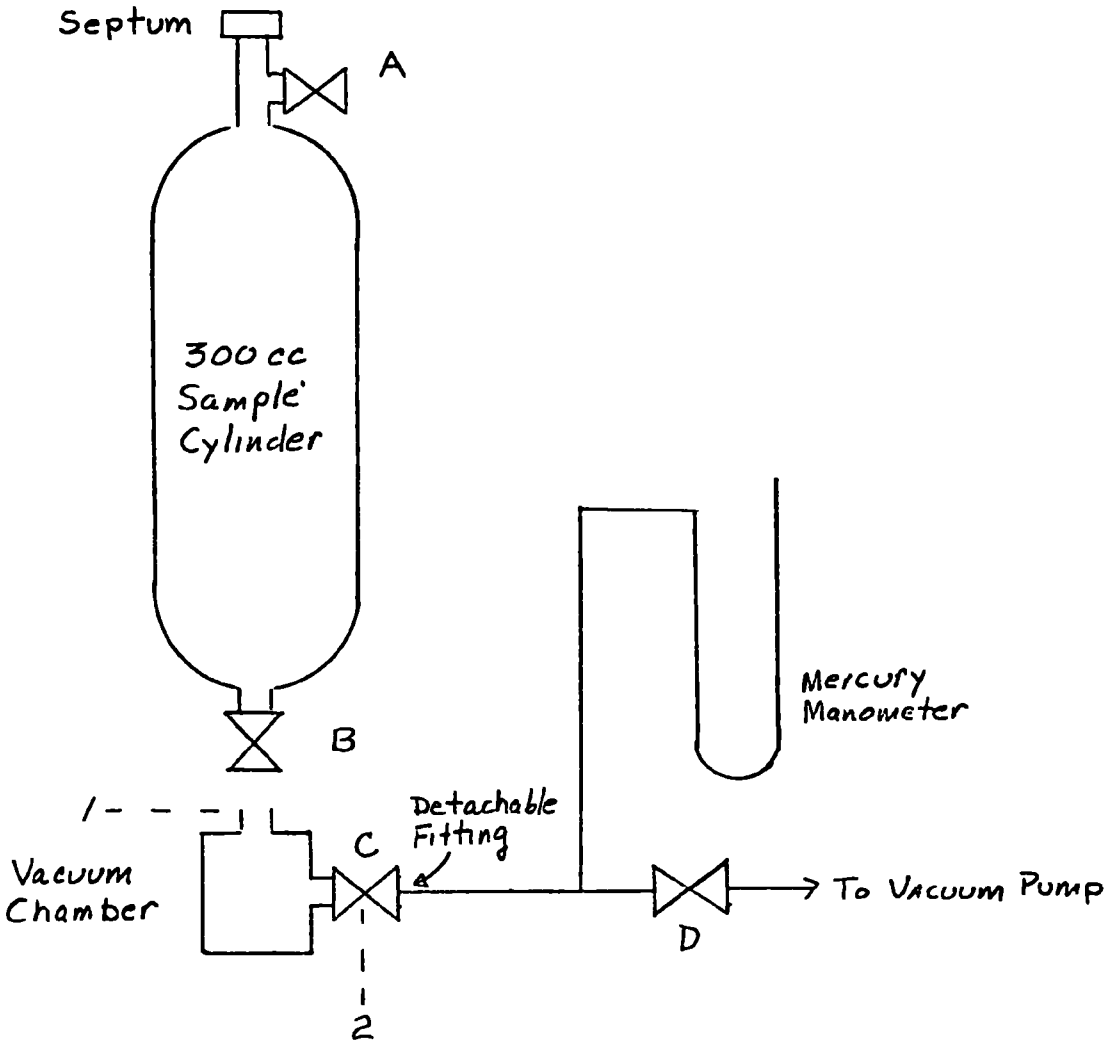

Septum
A
300 cc
Sample
Cylinder
B
Mercury
Manometer
Detachable
Fitting
C
Vacuum
Chamber
To Vacuum Pump
D
2

FIGURE 1

APPENDIX C

CHEVRON VAPOR COMPOSITION METHOD

Chevron

Chevron Research Company
A Standard Oil Company of California Subsidiary
576 Standard Avenue, Richmond, California
Mail Address P O Box 1627, Richmond, CA 94802

A. L. Grossberg
Vice-President

July 9, 1981

Mr. Robert J. Bryan
Supervising Engineer
Engineering Science
125 West Huntington Drive
P.O. Box 358
Arcadia, California 91006

Dear Mr. Bryan:

Recently, Mr. R. A. Farnham of my staff contacted you in response to your request to WOGA for industry assistance with your EPA contract involving vapor pressures of heavy crudes. At that time, he mentioned he had conceived a method which he believed to be superior to other methods under consideration. We are enclosing a report outlining the details of that method.

We recommend that the method outlined in the report should receive your careful consideration for further development. Although the method has not been tested in the laboratory, it has the potential of solving the difficult sampling and sample transfer problems associated with other methods listed in your letter to WOGA. The method also has other advantages:

1. It provides useful information on vapor composition for calculating total hydrocarbon and reactive hydrocarbon emissions.

2. The results are obtained at the temperature of interest.

If you have any questions regarding the above, please contact Mr. R. A. Farnham at (415) 237-4411, Ext. 4882.

Sincerely yours,

Encl. - Report, "Apparatus and Method for Determining Vapor Composition and Vapor Presssure of Heavy Stocks at 4:1 Ratio of V/L," above date

cc: Mr. R. N. Harrison

CHEVRON RESEARCH COMPANY
RICHMOND, CALIFORNIA

APPARATUS AND METHOD FOR
DETERMINING VAPOR COMPOSITION
AND VAPOR PRESSURE OF HEAVY STOCKS
AT 4:1 RATIO OF V/L

JULY 9, 1981

Author - R. A. Farnham

Sampling and analyzing heavy stocks for vapor pressure is difficult and in many cases impossible when using the Reid Vapor Pressure Test. The apparatus and method proposed herein resolves the problems associated with the above. Also, the results of the proposed method provide additional data which are directly applicable to emission calculations which pose the most frequent need for testing of heavy stocks.

The method using the apparatus described is not affected by the presence of water or dissolved air in the sample. The apparatus and method can be easily modified to give results at different ratios of V/L. The method involves use of the equipment shown on Attachment I.

Preparation for Sampling

Vessel A is first assembled as shown. Valve 2 is closed; the rest are open. The vessel is inverted so Valve 3 is uppermost. Water or other suitable liquid is introduced through Valve 4 until liquid overflows from Valve 3. All valves are then closed, and the vessel is ready for sample introduction.

Sampling

Vessel B (which is empty) is attached to Vessel A by screwing the close Nipple 5 into Valve 3. Valve 1 is then connected to the vessel to be sampled and then opened. Vessel B should be positioned so that it is vertical and Valve 6 is uppermost. Valve 6 should be opened and the air vented slowly until liquid appears in the gauge glass. Valve 6 should then be closed quickly. Then close Valve 1 and disconnect from source. Close Valve 3 and remove Vessel B.

Analysis

In the laboratory connect a 10-psig pressure gauge to Valve 2 and a nitrogen source regulated to 5 psig to Valve 1. Open Valve 3 and slowly pressurize with N_2 to 3 psig. Close Valves 3 and 1. Immerse Vessel A into a water or an oil bath at desired temperature. If after equilibrium is reached the pressure gauge reads less than 5 psig,

Encl. - Attachment I (RE 816349)

pressurize slowly with nitrogen to 5 psig. After equilibrium is reached, remove nitrogen source and withdrawn vapor sample from Valve 1 for injection to chromatograph. Read pressure gauge and temperature of bath.

Calculation and Reporting Results

From chromatograph analysis calculate the following:

1. Average Molecular Weight of Hydrocarbon (HC) in Vapor, Lb/Lb Mole, [A]

2. Molecular Fraction of HC in Vapor, [B]

3. Weight Fraction Reactive HC of Total HC in Vapor, [C]

Using above data and pressure gauge reading, the vapor pressure of the hydrocarbon at 4:1 V/L and bath temperature can be calculated.

$$VP)_T = [B] \times [\text{Gauge Reading} + \text{Barometric Pressure}]$$

Calculation of Emissions Using Results

Emissions can be calculated from a source at bath temperature and containing stock below its bubble point if the SCFH of vapor emitted from the source and the fractional approach to equilibrium [F] are known.

$$\text{Total HC Emissions, Lb/Hr} = [A] \frac{VP)_T}{\text{Barometric Pressure}} \times \frac{SCFH}{379} \times [F]$$

Reactive HC Emissions, Lb/Hr = [C] x Total HC Emissions

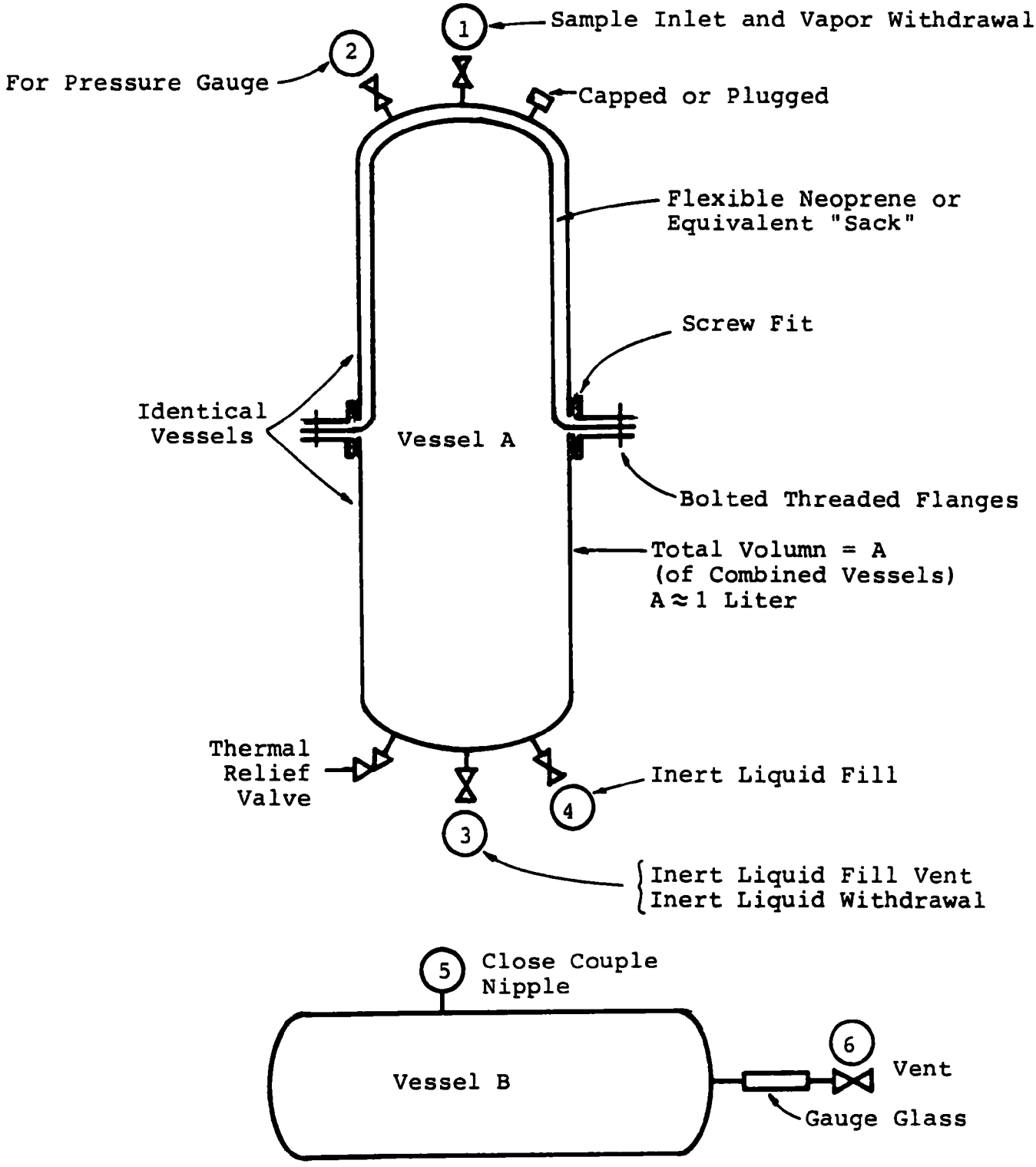
Special Cases

If the stock to be sampled is at high temperature, a mineral oil can be used in place of water. If cooling of the sample during sampling is a problem or if very precise V/L is required, mineral oil can be used and the apparatus containing oil can be heated to bath temperature (source temperature) before sampling. If heating is required, Valve 3 should be uppermost and partially open during heating .

:cd

ATTACHMENT I

APPARATUS FOR DETERMINING VAPOR COMPOSITION AND
VAPOR PRESSURE FOR HEAVY STOCKS AT
4:1 RATIO OF V/L



Volumn = 1/5 Volumn A

R. A. Farnham
CHEVRON RESEARCH COMPANY
PROCESS ENGINEERING DEPARTMENT
ENGR. RES. AND DEV. DIVISION
RAF 816349

APPENDIX D

EVAPORATION METHOD

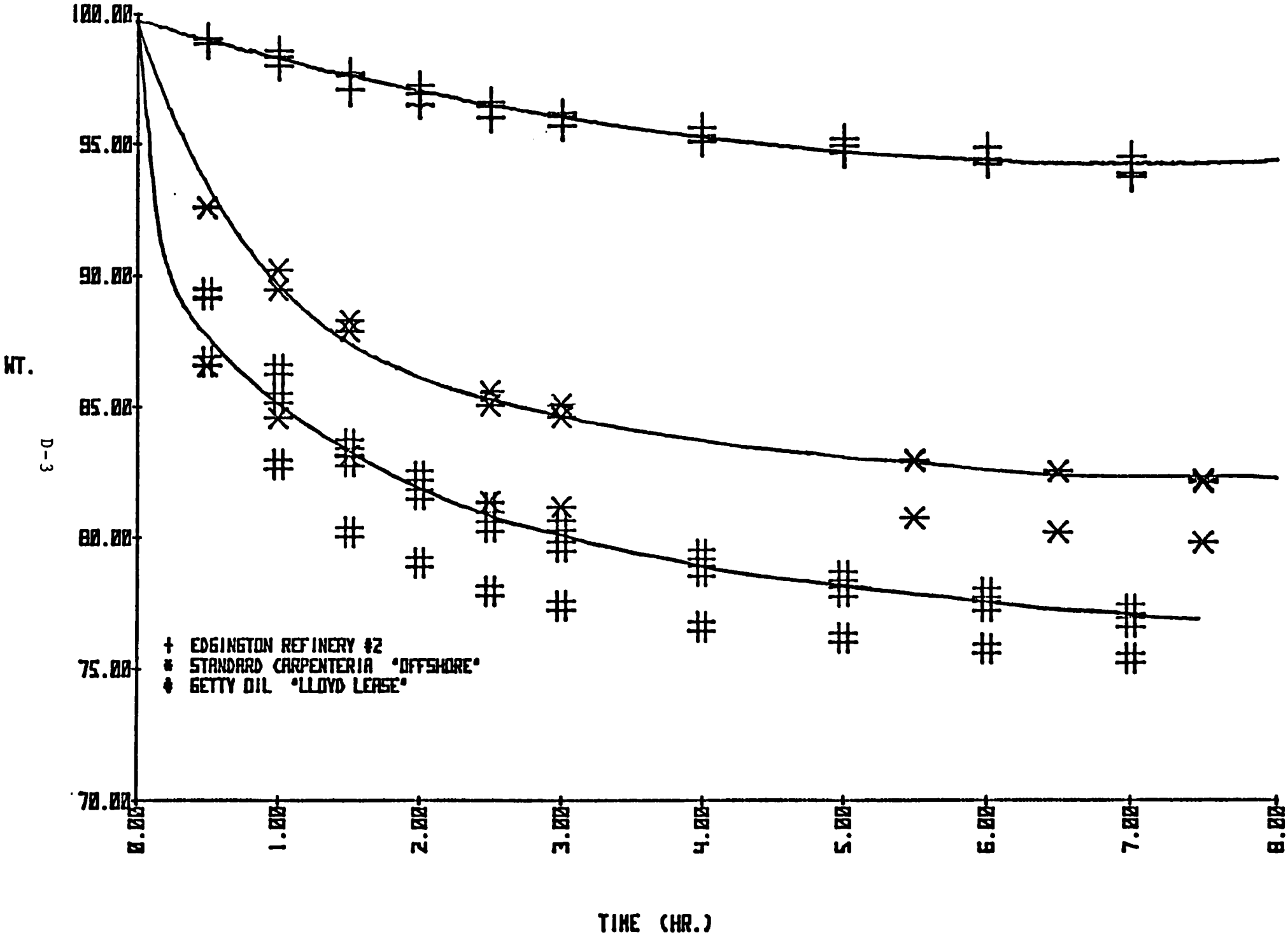
Characterization of Crude Oil

Procedure for Gravimetric Method

The weights of several petri dishes with lids were measured and recorded. In order to preserve a homogeneous sample, the crude was vigorously shaken before pouring to an approximate depth of 1/8" in three petri dishes. The dishes and lids containing the sample were again weighed and placed in a laboratory oven at 100°F. The oven was maintained at 100°F throughout the test. A small Thomas pump purged the oven (approx. val. 66 liters) at the rate of 2 liters/min. This small flowrate did not disturb the evaporation while keeping the percent of hydrocarbons at an insignificant value in the oven vapor space. The samples were removed from the oven and weighed at 1/2 hr. intervals at the start of the test. After approximately 2-1/2 hrs., the weight loss rate dropped to a value that allowed 1 hr. weighing intervals to be sufficient. The test was conducted for approximately seven hours. Upon completion of the test, weight loss and percent weight loss were calculated and plotted versus time.

COMPARISON OF
GRAVIMETRIC METHOD AND REID METHOD

Sample source	Percent weight Loss at 100° F			Reid Vapor Pressure at 100° F per Union Oil
	after 1 hr	after 2 hr	after 6 hr	
Conoco #66	98.9	97.7	94.4	0.4
Edgington Refinery #2	98.3	96.9	94.4	0.4
Conoco #35	96.4	93.2	87.1	0.6
Std Carpinteria offshore	89.4	86.5	82.7	4.0
Union shipping tank	88.1	85.6	82.2	2.9
Getty Oil Loyd Lease	85.3	81.6	77.4	5.2
Arco RRU #6	81.7	77.9	73.0	3.8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80.00
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70.00
WT.
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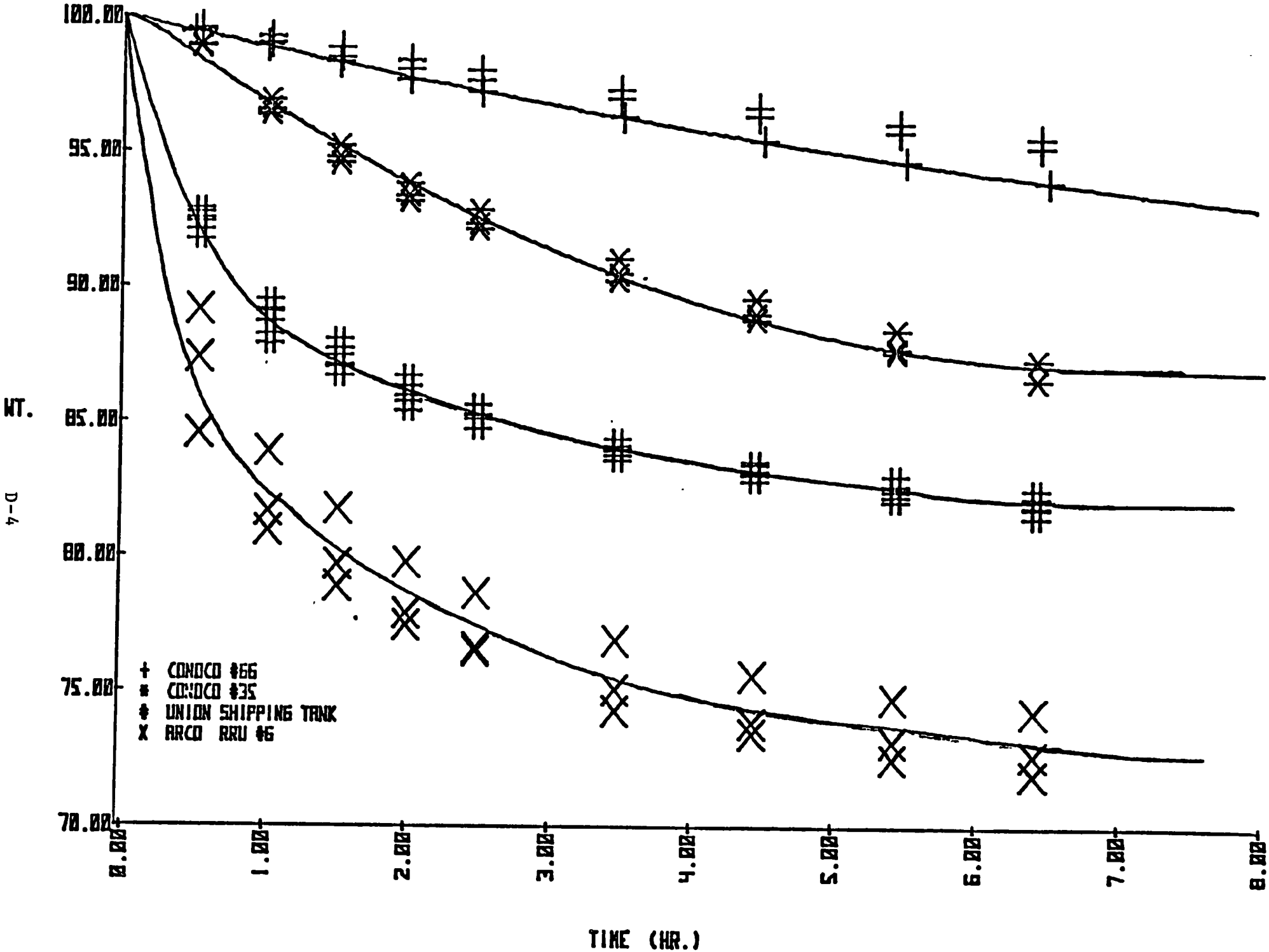
4.00
5.00
6.00
7.00
8.00
TIME (HR.)
+ EDGINGTON REFINERY #2
* STANDARD CARPENTERIA "OFFSHORE"
# GETTY OIL "LLOYD LEASE"


100.00
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3.00
4.00
5.00
6.00
7.00
8.00
TIME (HR.)
+ CONOCO #66
# CONOCO #35
* UNION SHIPPING TANK
X ARCO ARU #6

APPENDIX E

EQUIPMENT COSTS

APPENDIX E

EQUIPMENT COSTS

Costs are estimated for specialized and laboratory equipment to conduct the standard Reid Vapor Pressure (RVP) test and the vapor composition test. In the case of the RVP test, a container is required for each sample collected at the same time. The RVP "bomb" apparatus is used only during the analysis, but several bombs may be needed to avoid delay in analysis caused by the need for cleaning the apparatus. Sample containers used for the vapor composition method are considerably more expensive than those used for RVP testing but are close in cost to the RVP bombs. Unit cost estimates are given in all cases.

Only significant items of equipment are included in our estimate. No attempt was made to estimate the number of sample containers or RVP bombs needed. Costs are summarized in the attached table.

SUMMARY OF EQUIPMENT COSTS

Cost Item	Reid Vapor Pressure	Vapor Composition
Laboratory Equipment		
(1) Bath, Constant Temperature (Thelco 261)	$545.00	
(2) RVP Bomb per ASTM D323-72 (VWR 51864-029)	345.00 ea.	
(3) Pressure Gage 0-5 psi ± 0.1 psi per ASTM D323-72 (VWR 51869-022)	156.95 ea.	
(4) Gas Chromatograph, single column, FID, with linear temperature program (Varian 1440)		$5030.00
(5) Gas Chromatograph Data System (Varian CDS-III and chart recorder)		4845.00
(6) Flow meter, valves, flow controller, filters, regulators for gas chromatograph		930.00
Field Equipment		
(1) Cooling Bath per ASTM D270-2546	200.00 ea.	
(2) Sample Containers, RVP samples	50.00 ea.	
(3) Sample containers, Chevron vapor composition procedure		600.00 ea.

50272-101

REPORT DOCUMENTATION PAGE	1. REPORT NO. EPA 909/9-81-004	2.	3. Recipient's Accession No

4. Title and Subtitle

Analysis of Potential Methods to Determine the Volatilities of Heavy Crude Oils

5. Report Date: December 1981

6.

7. Author(s): Robert J. Bryan

8. Performing Organization Rept. No: 9211.00

9. Performing Organization Name and Address

Engineering-Science, Inc.
125 West Huntington Drive
Arcadia, CA 91006

10. Project/Task/Work Unit No.: W. A. 11

11. Contract(C) or Grant(G) No
(C) 68-02-3509
(G)

12. Sponsoring Organization Name and Address

U.S. Environmental Protection Agency, Region IX
215 Fremont Street
San Francisco, CA 94105

13. Type of Report & Period Covered: Final Report

14.

15. Supplementary Notes

16. Abstract (Limit 200 words)

This report covers the investigation of possible alternative methods to measure the volatility of heavy crude oil. The work was restricted to a literature search and inquiries made to informed government and industry groups. The current method for determining vapor pressure at storage temperature for crude oil and refined petroleum products involves determination of Reid Vapor Pressure and use of a correlation nomograph. The technique is not applicable to some heavy crudes. Also, there can be an undue influence from methane and ethane.

Alternative methods investigated include developing data to extend the temperature and vapor pressure range of the correlation nomograph, modifying the Reid Vapor Pressure Method, use of a vapor composition approach, and determining evaporation losses under controlled conditions. Sampling and analytical problems were evaluated for the alternatives. A recommendation was made to conduct further studies on the vapor composition method.

17. Document Analysis a Descriptors

Crude oil, vapor pressure, Reid Vapor Pressure, volatility, evaporation loss.

b. Identifiers/Open-Ended Terms

c. COSATI Field/Group

18. Availability Statement	19. Security Class (This Report) Unclassified	21. No of Pages
	20. Security Class (This Page) Unclassified	22. Price

(See ANSI-Z39.18) *See Instructions on Reverse*

OPTIONAL FORM 272 (4-77)
(Formerly NTIS-35)
Department of Commerce