

# CHROMATOGRAPHIC DETERMINATION OF GUM IN FUELS

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*MARCH 1955*

MATERIALS LABORATORY  
CONTRACT No. AF 18(600)-37  
PROJECT No. 3048

WRIGHT AIR DEVELOPMENT CENTER  
AIR RESEARCH AND DEVELOPMENT COMMAND  
UNITED STATES AIR FORCE  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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## FOREWORD

This report was prepared by the Shell Development Company, under USAF Contract No. AF 18(600)-37. The contract was initiated under Project No. 3048, "Aviation Fuels", Task No. 73300, "Fuel Stability" formerly RDO No. 601-301, "Aircraft Fuels and Lubricating Oils", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. R. W. Sneed acting as project engineer.

This report is the second part of WADC TR 54-328. The first part of this report was published in September 1954 under the basic report number only; it should be considered as Part I although it was not so marked.

WADC TR 54-328  
Part II

ABSTRACT

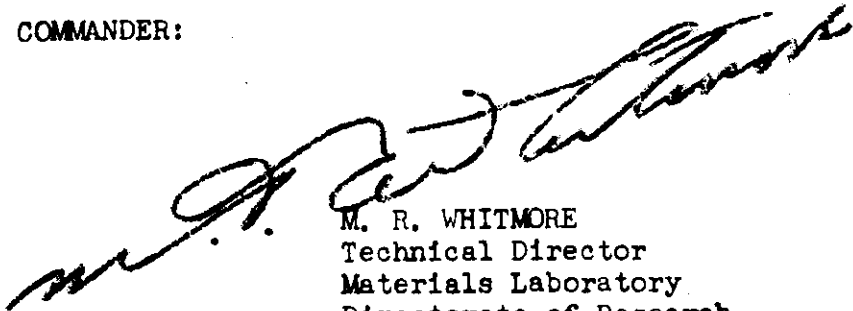
A novel method for the determination of soluble gum in jet fuel, gas oil and possibly also in gasoline was introduced in a previous WADC TR 54-328. The gum content is related to the length of a brown zone observed when the fuel is displaced over silica gel in a small chromatographic column with  $\alpha$ -methylnaphthalene as solvent and acetone as eluent. This method is superior to the conventional procedure involving evaporation at elevated temperatures in a jet of steam because it is much simpler and permits the use of very small samples which is advantageous in research work on fuel stability.

The present, supplementary report deals with improvements of this "chromatogum" method. The purification of  $\alpha$ -methylnaphthalene has been made more effective, the necessity of using a closely specified amount of sample has been eliminated, and a narrower column has been designed to improve the reliability even though smaller samples are employed. Also, the method appears to be applicable to insoluble gum from jet fuels and many gas oils.

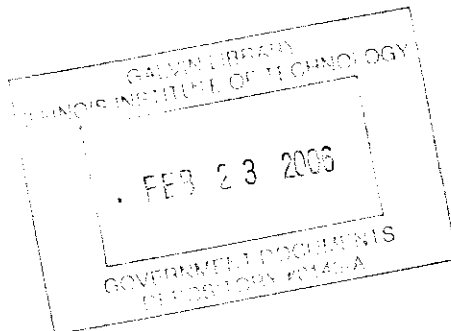
PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. WHITMORE  
Technical Director  
Materials Laboratory  
Directorate of Research



WADC TR 54-328  
Part II

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## CHROMATOGRAPHIC DETERMINATION OF GUM IN FUELS (II)

### Introduction

A previous report introduced a novel chromatographic method for determination of gum in various fuels (WADC Technical Report 54-328). In that report were described some of the variables affecting the relation between gum content and length of a brown zone observed where the fuel is displaced over silica gel with  $\alpha$ -methylnaphthalene (MN) as solvent and acetone as eluent.

In this report, which is supplementary, additional data obtained by the method are discussed and it is pointed out that MN of the specified purity contains appreciable amounts of gum and that it deteriorates on storage. When more carefully purified MN was used, the zone length observed with high gum samples was shortened disproportionately. Furthermore, in order to avoid diffuse gum zones, it was necessary to reduce the pressure from 5 to 3 psi, and this resulted in further shortening of the zone length. For these reasons the column was redesigned, resulting in improved reliability with smaller samples than formerly required. The revised method, EMS 6M2/54a, is presented in the Appendix.

### Improvement of the Chromatogum Method

#### Purification of $\alpha$ -methylnaphthalene

The Eastman "practical" grade  $\alpha$ -methylnaphthalene (MN) used as solvent for the gum concentrated on the silica gel column is very dark, and in the early work it was decolorized by a simple chromatographic step. The treated material still contained excessive amounts of gum and deteriorated on storage for a week or two at room temperature in the presence of light and air. In the hope of obtaining very stable, gum-free MN, a portion was purified by performic acid oxidation to remove sulfur and nitrogen compounds, followed by chromatography to remove the oxidation products. The purified MN was water white and very low in sulfur, nitrogen, and gum, but was only relatively stable. Meanwhile an improved chromatographic decolorization for the unpurified MN was developed which produced a satisfactorily gum-free solvent, and since this technique is simple it was adopted as described in EMS 6M2/54a in the Appendix. All data in the present report were obtained with MN having a blank of about 5 mm (15 mm in the new narrower column to be described).

Purifying the MN had a disproportionate effect on the zone lengths observed with fuels of high gum content, which tended to reduce the zone length difference between high and low gum samples, thus reducing the accuracy. This was later compensated by changing the column design.

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## Effect of Sample Size

While in the early work it appeared to be necessary to standardize on the sample size, it has now been found that any amount can be used provided the resulting brown zone is of suitable length, or about 25 to 150 mm. In the present report the length of the brown zone is correlated graphically with the known steam jet gum content of the sample and expressed in milligrams instead of milligrams/deciliter as before, and the resulting plots are independent of sample size.

## Effect of Pressure

In the previous report it was stated that as the pressure increases the length of the brown zone increases. Accordingly it was recommended that the pressure be varied, depending on the type of sample, so that the brown zone length could be converted to gum content by means of a single graphical correlation. In practice it has proved better to employ a constant pressure and several graphs for the various fuel types. A pressure of 3 psi was selected as the maximum at which the brown zones do not become too diffuse in the upper part of the column. Also, at 3 psi the zones in the Analyzer or capillary section are sharper than at higher pressures.

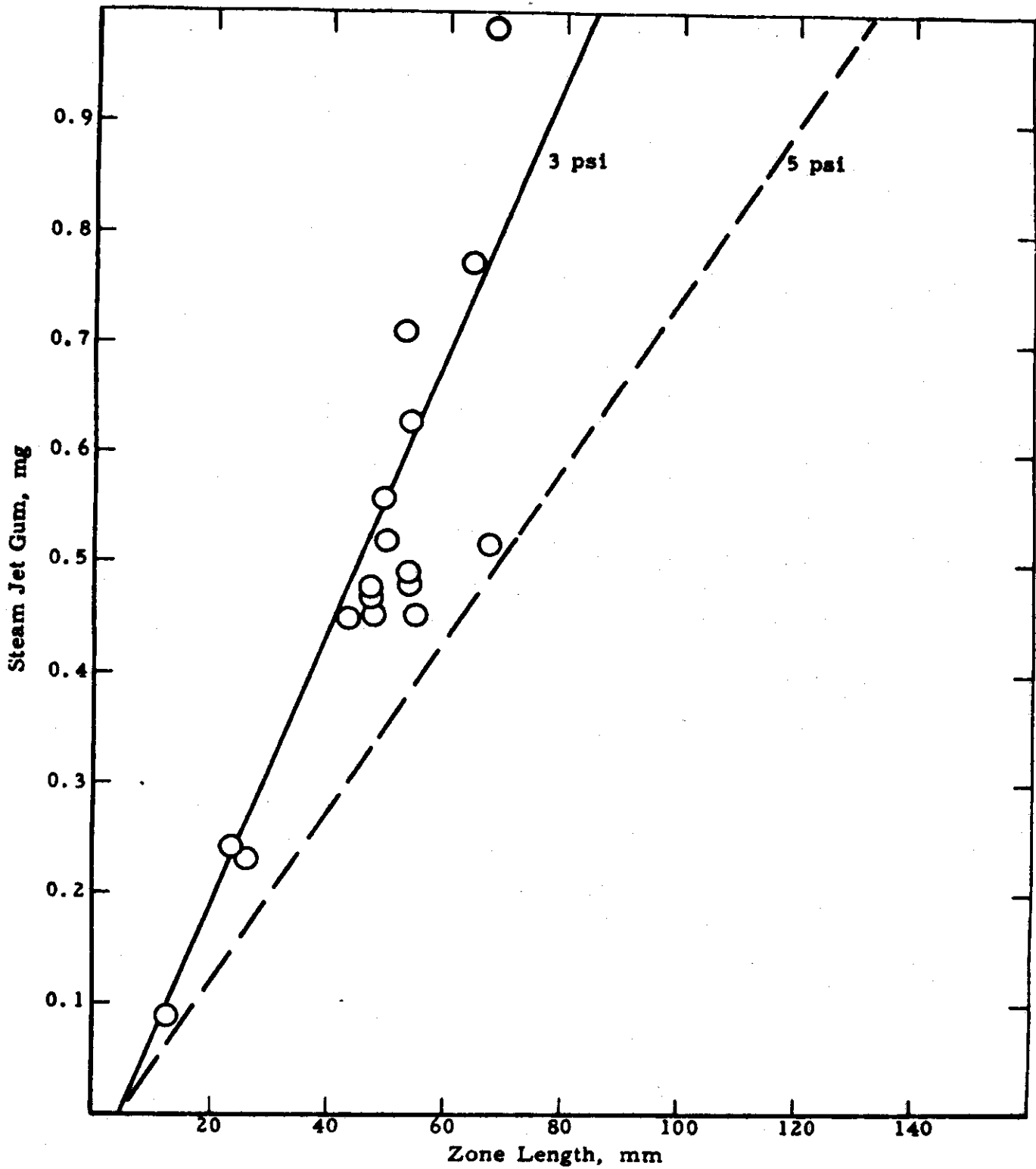
Gas oil and jet fuel chromatogum data obtained in the old column at 3 psi are shown in Figures 1 and 2, respectively, together with lines representing data at 5 psi. Although straight lines have been drawn through the points, it is possible that if more data were available a curve would provide a better fit, as was the case with JP-4 jet fuels analyzed at 5 psi (Figure 2). The zone length at 3 psi changes less rapidly with gum content than at 5 psi, resulting in some decrease in accuracy in the large column even though the zones were sharper at the lower pressure.

## Effect of Storage Conditions

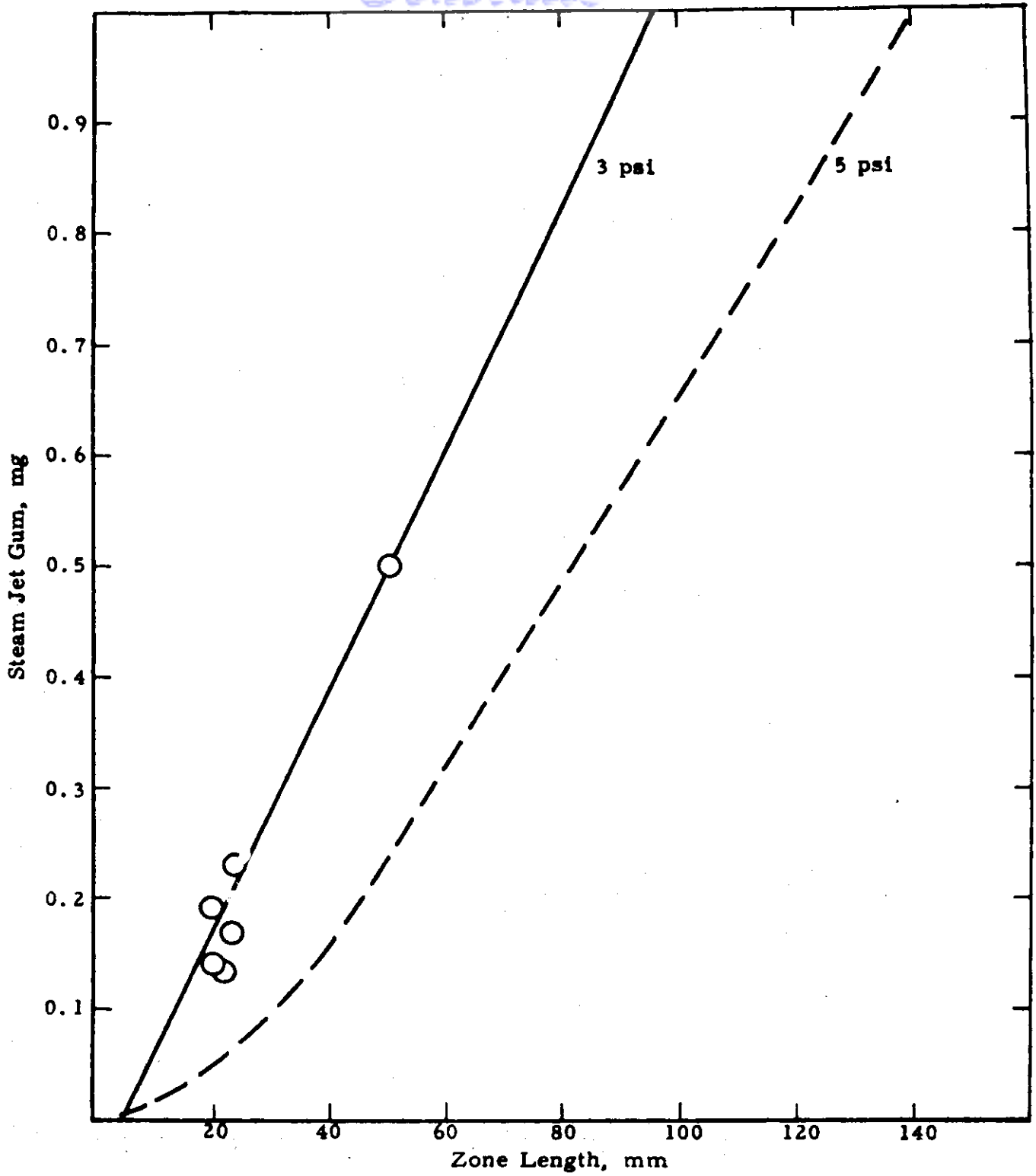
The data plotted in Figure 1 represent gas oils stored in a constant temperature room at 110°F (43°C) and analyzed in the old, wider column at 3 psi, while the dotted line is based on gas oils stored at 70°C and analyzed at 5 psi. The difference is due mainly to the pressure employed during the analysis, since a similar effect is shown in Figure 2 where both curves are for desert storage conditions. Thus the evidence indicates that gas oils stored at temperatures up to 70°C may be analyzed by the chromatogum method. Study of gas oils aged at 100°C showed that a much steeper curve was obtained, so steep in fact that the method was virtually inapplicable. This situation was improved somewhat by the change in column design, discussed below.

A few jet fuels that had been subjected to accelerated aging were studied, and the data indicate that the steam jet gum-chromatogum correlation for jet fuels, as shown in Figure 2, is valid up to an aging temperature of 100°C.





**Figure 1. CHROMATOGUM ANALYSES FOR SOLUBLE GUM IN GAS OILS  
OLD COLUMN (1.6 mm)**



**Figure 2. CHROMATOGUM ANALYSES FOR SOLUBLE GUM IN JP-4 JET FUELS  
OLD COLUMN (1.6 mm)**

In order to compensate for the decreased gum zone length resulting from more careful decolorization of the MN and reduction of the pressure from 5 to 3 psi, the inner diameter of the Analyzer section of the column was reduced from 1.6 to 1.0 mm. Chromatogum data for the new column, plotted in Figures 3 and 4, show, by comparison with Figures 1 and 2, that for a given amount of gum the zone is more than doubled. In addition the sharpness is improved, and it is felt that the precision and accuracy are better in the new column even if the sample volume is halved. The standard deviation between steam jet gum and chromatogum values has been improved from 16% to 12% for gas oils and jet-fuels (Figure 1, WADC TR 54-328 compared with Figures 3 and 4).

The correlation between steam jet gum and chromatogum in the case of gas oils aged at 100°C was improved using the new column, and the chromatographic method is now suitable for a rough gum determination on these samples. Assignment of a numerical correlation is not possible with the limited data available.

#### Insoluble Gum

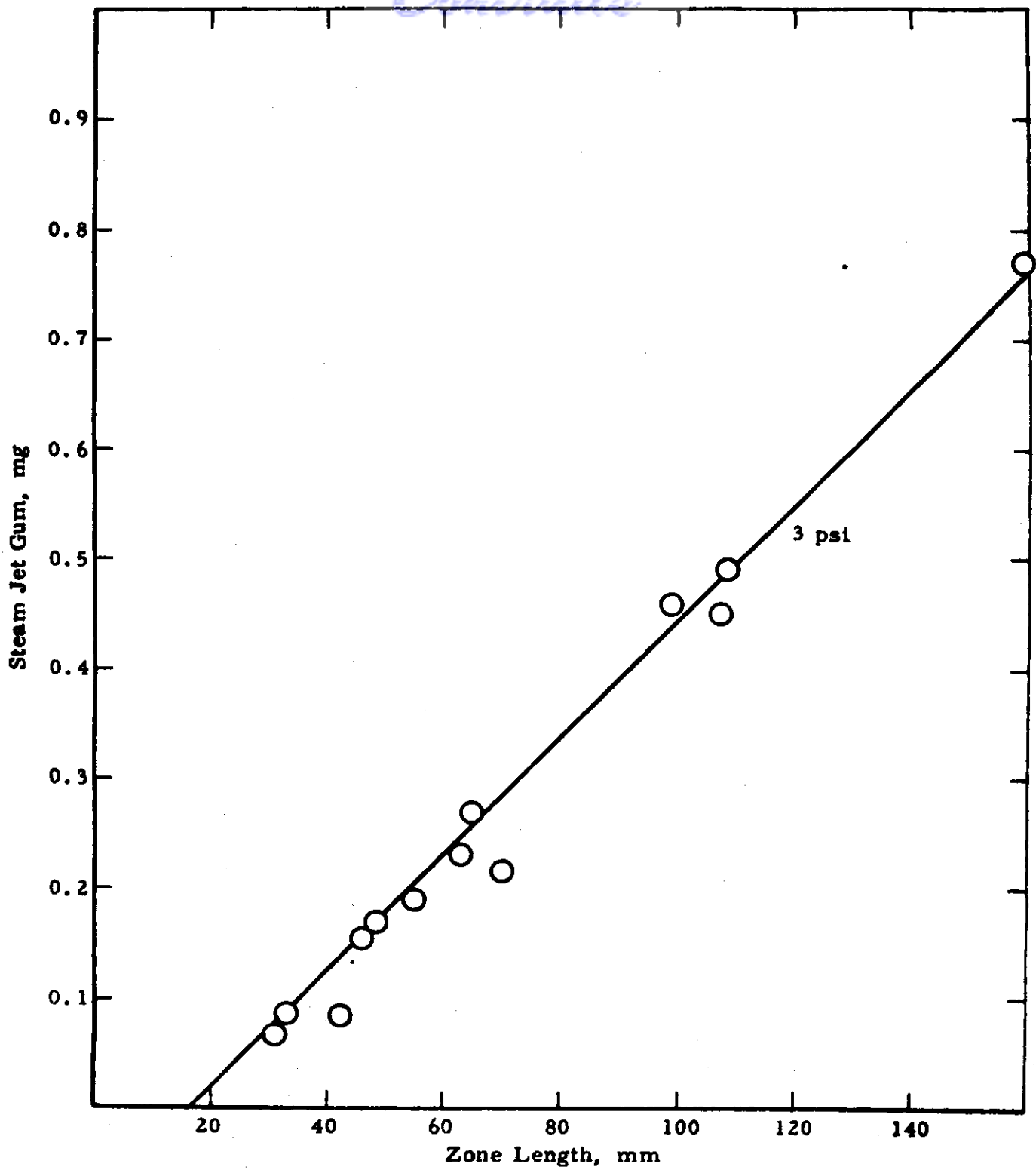
By definition, insoluble gum is the material retained on a "fine" (Pyrex Brand) sintered glass filter when the fuel is filtered and the precipitate is washed with n-hexane. The gum thus isolated is dissolved in a polar solvent mixture (methanol, ethyl acetate and benzene, 1:1:1) and sampled for the chromatogum determination. The solvents are removed by evaporation and the residue washed into the silica gel column with chloroform. Thereafter the procedure is the same as for soluble gum.

In the case of jet fuel meager data suggest that the same curve can be used for both soluble and insoluble gum. More extensive data on gas oils using the old and new columns are shown in Figures 5 and 6, respectively. Most of the points far to the right of the line in Figure 5 are for high molecular weight gas oils, indicating that these must be correlated separately or that their scatter is unusually bad. No such divergence is apparent in Figure 6, but here the high molecular weight fractions were low in gum, and hence the two sets of results are not conflicting.

#### Recovery of Gum-Free Samples

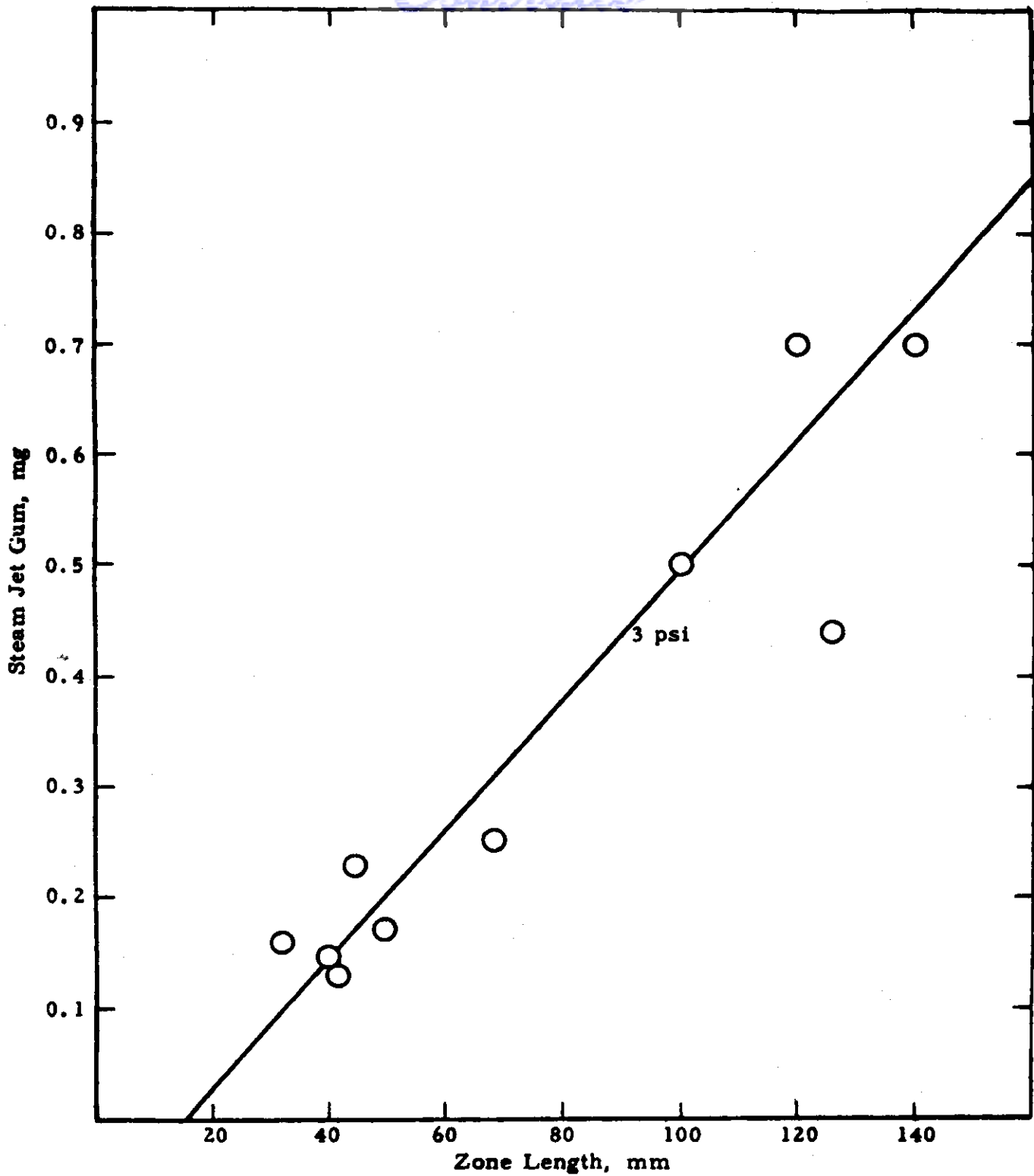
In the previous report it was mentioned that isopropyl chloride could be used as a gum solvent in place of MN. In the course of this work it was found that isopropyl chloride displaced the hydrocarbon components of the fuels practically completely while leaving the gum adsorbed on the column. Thus isopropyl chloride could serve as a buffer between the gum and the rest of the sample. By diluting 1 ml of fuel with an equal volume of isopropyl chloride, displacing the mixture through the column and evaporating off the chloride, it was possible to recover the gum-free hydrocarbons for further study.

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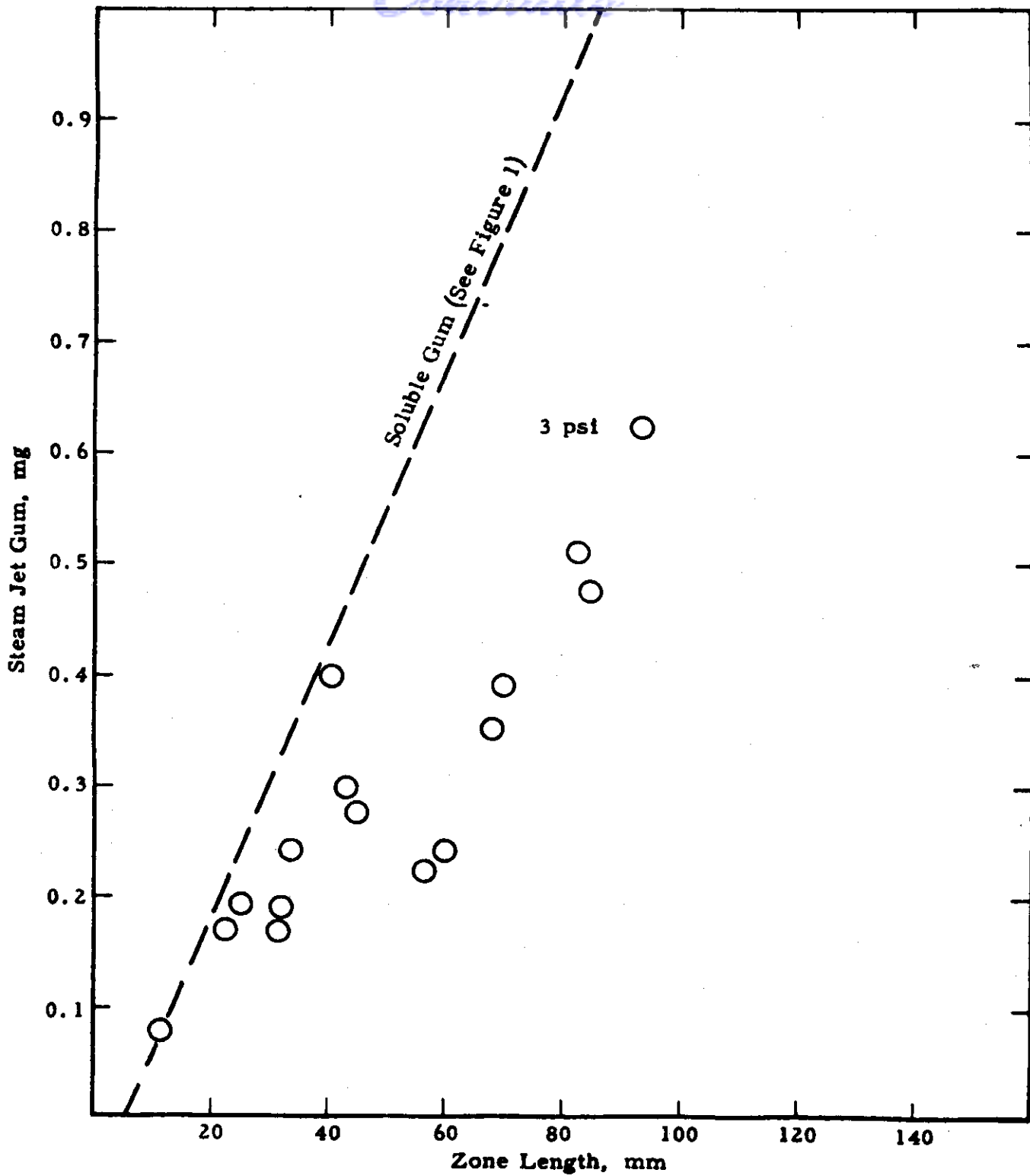
**Figure 3. CHROMATOGUM ANALYSES FOR SOLUBLE GUM IN GAS OILS  
NEW COLUMN (1.0 mm)**

*Controls*

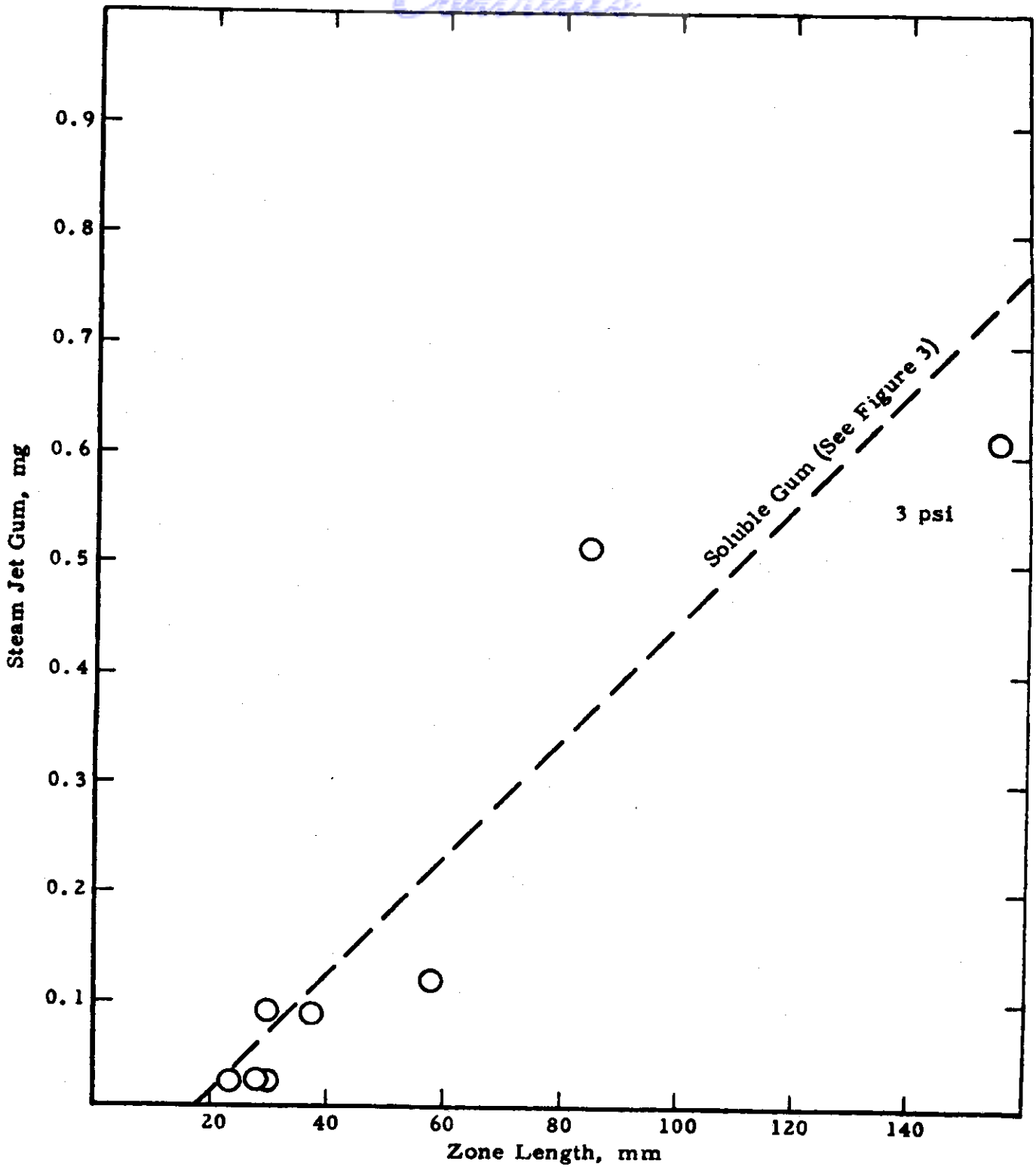


**Figure 4. CHROMATOGUM ANALYSES FOR SOLUBLE GUM IN JP-4 JET FUELS  
NEW COLUMN (1.0 mm)**

Continued



**Figure 5. CHROMATOGUM ANALYSES FOR INSOLUBLE GUM IN GAS OILS  
OLD COLUMN (1.6 mm)**



**Figure 6. CHROMATOGUM ANALYSES FOR INSOLUBLE GUM IN GAS OILS  
NEW COLUMN (1.0 mm)**

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## Conclusion

The chromatogum method has been improved by specifying 1) more careful purification of the MN, 2) constant pressure for fuels of all types with interpretation of the results according to type, and 3) a new, narrower column which gives improved precision with smaller samples. By a similar technique, insoluble gum can also be determined. The correlation between steam jet and chromatogum is poor for both soluble gum from gas oils aged at 100°C and insoluble gums from gas oils boiling above approximately 275°C.



SHELL DEVELOPMENT COMPANY  
ANALYTICAL DEPARTMENT 1)

## Determination of

SOLUBLE GUM IN FUELS  
CHROMATOGRAPHIC METHODSCOPE

1. This method describes a procedure for the determination of soluble gum in JP-4 jet fuels and gas oils boiling up to about 310°C (585°F). The gum values correspond to those obtained by steam-jet evaporation at 500°F.

METHOD SUMMARY

2. A small glass adsorption column is packed with fine, activated silica gel and one half to two milliliters of sample is introduced; benzene-free samples are first diluted with benzene. The sample is followed by a small quantity of  $\alpha$ -methyl-naphthalene and then acetone as eluent. The length of a brown zone containing the gum is measured and empirically correlated with the steam-jet gum content.

APPARATUS

3. (a) Adsorption Column, made of glass and consisting of a Charger section, a Separator section, and an Analyzer section, as shown in Figure 1. Analyzer section true-bore tubing is available from Rankin Glassblowing Company, Martinez, California.

Note 1. A pipe manifold with a series of inner spherical joints for the columns makes a convenient arrangement. (See Figure 1, SMS 644/52).

(b) Hypodermic Tubing, No. 21 Stubs gage, about 50 cm long with a 45° angle tip and sealed into a short section of copper tubing and connected to tap water.

(c) Vibrator for packing the adsorbent, such as the Vibrosage, model BV, 110 V, 60 cycle, available from Beauty Appliance Corporation, Racine, Wisconsin.

MATERIALS

4. (a) Silica Gel, Grade 923 (100 to 200 mesh), from the Davison Chemical Corporation, Baltimore, Maryland.

(b) Acetone, 99+%.

(c)  $\alpha$ -Methylnaphthalene, Eastman practical grade, purified by passing it over a Grade 923 silica gel column using acetone as eluent, and discarding the brown material. For example, 25 to 50 ml can be decolorized

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1) This method is written for departmental use and needs. Extension of the method to other applications requires critical examination.

on a column holding 20 grams of gel and having a lower section of 5 mm inner diameter and 350 mm length. Run a blank on the product according to the procedure below; if a faintly brown zone of more than 15 mm is observed, repeat the purification. Store the solvent in the cold.

(d) Pressuring Gas, air or nitrogen, delivered to the top of the column at a regulated pressure of 0 to 10 psi.

(e) Plasto Orange RS Indicator Dye, from Allied Chemical and Dye Corp., National Aniline Division, San Francisco, California. Make up indicator dye on silica gel by slurring 0.10 g dye and 100 ml gel with methanol. Evaporate the solvent at room temperature in a stream of air, stirring occasionally, until the dyed gel is free-flowing.

### PROCEDURE

5. (a) Put a cotton plug in the tip of the column and fill it with silica gel, applying the rubber-padded vibrator as needed until the packed silica gel is 30 to 40 mm below the top of the Separator section. If the sample is light colored, or when determining the blank, add 10 mm of dyed gel.

Note 2. The gel may be re-screened through a 60 mesh sieve if desired, to remove occasional coarse particles that may plug the Analyzer section.

(b) Introduce the sample, as follows:

1) If the estimated gum content is above ca 30 mg/dl use  $0.50 \pm 0.03$  ml, otherwise use  $1.00 \pm 0.05$  ml; however, any convenient volume in this range can be used.

2) If the benzene + toluene content of the sample is less than 10%, or is not known, mix two volumes of sample with one volume of benzene, and use 1.50 or 0.75 ml of this solution. To conserve fuel, the dilution may be made in the top of the column by adding the benzene and immediately following it with the sample; in this case the amount of benzene used is not critical.

(c) Apply a pressure of 3 psi until the liquid front reaches the middle of the analyzer section; then the pressure may be increased to a maximum of 10 psi, depending on the volume and viscosity of the sample. (If too much pressure is applied, the zone will be askew). When the sample is taken up, add 0.10 ml of  $\alpha$ -methylnaphthalene and rinse the walls carefully with a few drops of acetone. Fill the charger with acetone, and apply pressure as above until the bottom of the brown zone reaches the top of the Analyzer; then reduce the pressure to 3 psi.

(d) After the top of the brown zone has progressed 100 to 150 mm into the Analyzer, take readings against a white background as follows: measure from the highest point of strong brown or yellow color to the lowest

point where color change is still apparent. Usually the column will be white below the brown zone, but sometimes it may be uniformly yellow. Ignore any discoloration of the gel in the Separator. Repeat the reading at 20 to 30 mm intervals until the zone length is stable.

(e) Disconnect the column, rinse out the gel with a jet of water from the hypodermic tubing, rinse with acetone and dry. Alternatively, after the gum is washed out, dry the gel by passing air through it and remove it by inverting and tapping the column.

Note 3.  $\alpha$ -Methylnaphthalene is a primary skin irritant and must therefore be handled with care; thus it is necessary to provide some means of collecting the effluent from the column.

## CALCULATION

6. Convert the length of the brown zone to steam-jet gum content as follows:

(a) For Gas Oils,

$$\text{Gum, mg/dl} = \frac{100}{V} (0.0054 L - 0.1)$$

(b) For JP-4 Jet Fuels,

$$\text{Gum, mg/dl} = \frac{100}{V} (0.0061 L - 0.1)$$

where

V = Volume of sample, ml, and

L = Length of brown zone, mm.

Note 4. Similar expressions may be obtained for other fuels and insoluble gum as data become available for these systems by plotting known gum contents against corresponding zone lengths and deriving the equation for the best straight line drawn through the points.

## PRECISION

7. Repeatability. Duplicate results by the same operator should be considered suspect if they differ by more than 10% of the value.

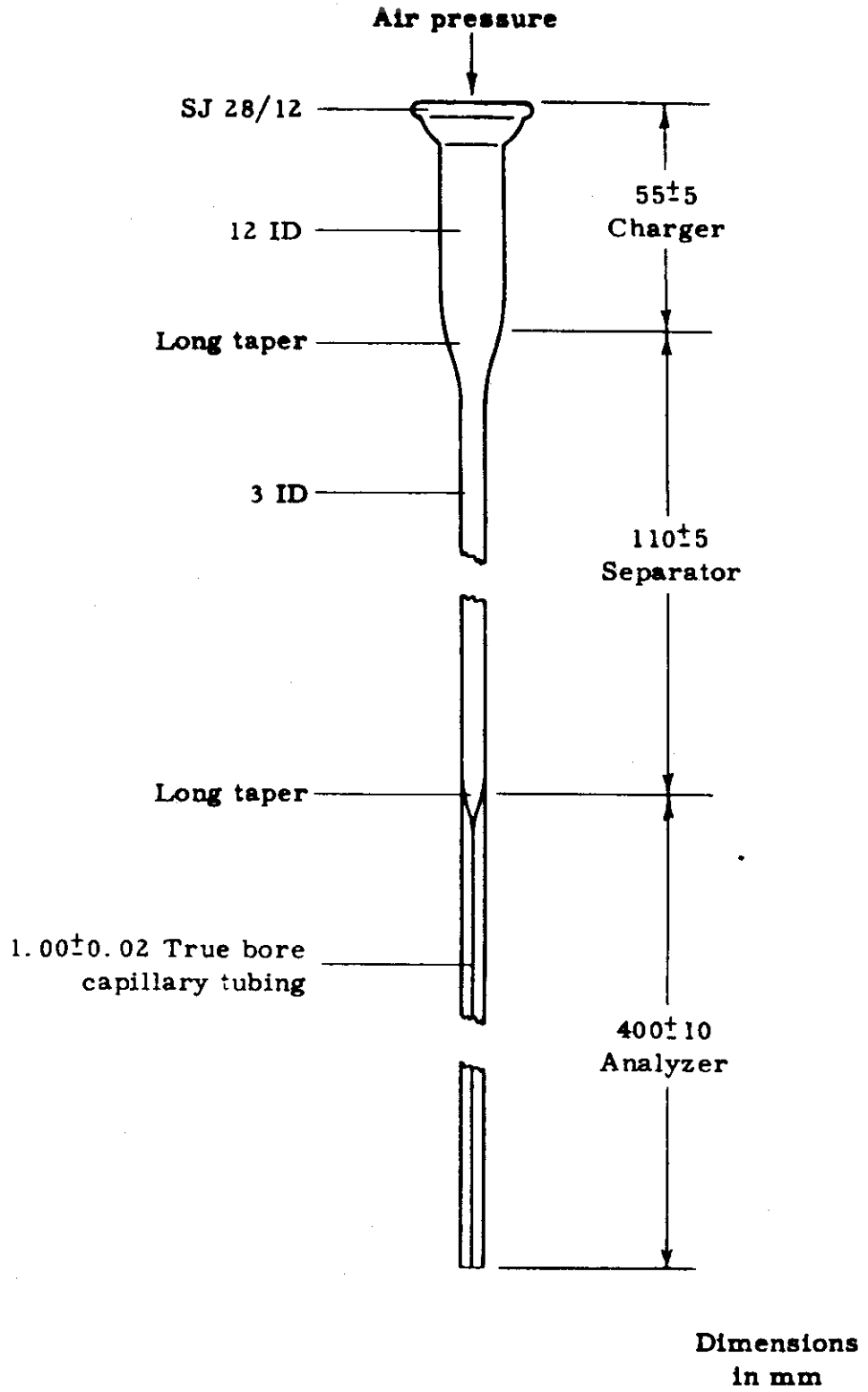


Figure 7. ADSORPTION COLUMN