

CHROMATOGRAPHIC DETERMINATION OF GUM IN FUELS

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Contracts

FOREWORD

This report was prepared by the Shell Development Company, under USAF Contract No. AF 18(600)-37. The contract was initiated under Research and Development Order 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 O. M. Ballentine acting as project engineer.

This report is not a supplement to Technical Report 53-63 prepared under this contract as it is a special report on a method development to measure gum in fuels by chromatographic determination.

WADC TR 54-328

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ABSTRACT

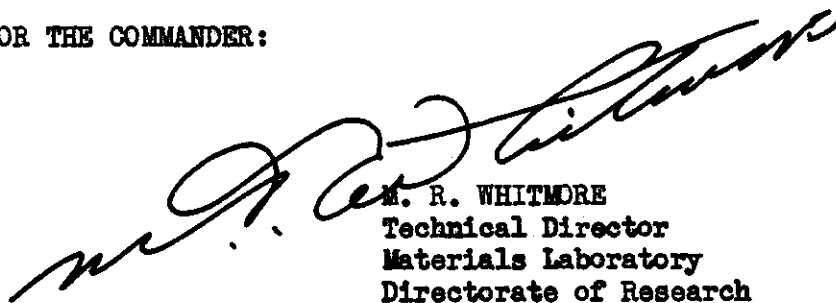
A chromatographic method of determining gum in small samples has been developed in order to solve problems in the investigation of jet fuel stability being carried out for the Air Force. Although the method was primarily intended for use with experimental fuels and components of limited availability, the simplicity, rapidity and ease of application may make it attractive under other circumstances.

The present introductory report deals with the use of this method with jet and diesel fuels and light fuel oils where its agreement with current procedure is adequate. Preliminary data suggest it may also be applicable to gasolines. Further investigation of the method is in progress to establish optimum procedures.

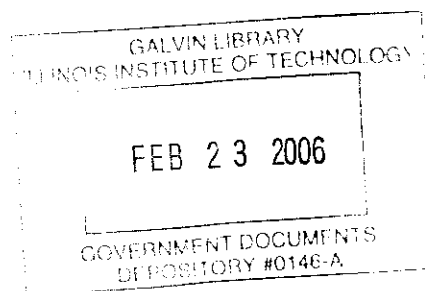
PUBLICATION REVIEW

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

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Chromatographic Determination of Gum in Fuels

Introduction

Fuel deterioration during storage in the presence of air results in the formation of various oxidized products which leave a gummy brown residue on evaporation. Prevention or minimization of gum formation is a continuing problem which is particularly severe with cracked fuels. The problem is becoming more acute as our dependence on cracked fuels increases and the engines in which the fuels are consumed become more complex.

The gum content of fuels is normally determined by evaporation of a 50-ml sample of fuel at elevated temperatures in a jet of air or steam. The residue is weighed and the gum content is reported in milligrams per deciliter (100 ml), mg/dl. This method is tedious, requires special equipment and relatively large amounts of fuel, and frequently gives inconsistent results. The fuel volume requirement is not significant normally but becomes important in studies on experimental or salvaged fuels of limited availability. Thus, in our Air Force contract^{a)} work on the fundamentals of jet fuel stability it was difficult to proceed satisfactorily in the absence of a method for gum determination on very small volumes of fuels.

Since small scale chromatography has become a very useful tool in hydrocarbon group analyses, the possibility of applying this technique to gum determination was considered. Initial experiments indicated that this approach was rather promising and therefore the work was pursued. This report introduces the proposed chromatographic method (EMS 6M2/54 in the Appendix) which has been found suitable for a wide variety of jet fuels as well as for gas oil. Incomplete data suggest that it may also be applied to gasoline.

Development of the Method

A jet fuel sample had been divided and one portion had been artificially aged with oxygen at elevated temperature to increase its gum content. These samples were subjected to chromatography to see whether zones were obtained that could be related to the gum contents. It was found that when the usual quantity of sample, about 1 ml, was added to a FIA column (Fluorescent-Indicator Adsorption, see SMS 644/52; a modified column is shown in Figure 1 of EMS 6M2/54 in the Appendix) of Davison's Grade 923 silica gel and displaced by isopropyl alcohol a brown zone was formed adjacent to the alcohol front. This zone was unexpectedly quite long for the small amount of gum present, but its length was approximately proportional to the gum content. Thus the feasibility of the chromato-

a) Contract No. AF 18(600)37 sponsored by the Materials Laboratory, Wright Air Development Center.

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graphic approach was indicated. Additional samples of jet fuels, as well as samples of gasolines and gas oils, covering the range of gum concentrations of interest, were obtained for study of the variables affecting the analysis and to aid in delineating its limitations.

Eluents

Eluents studied include isopropyl amine, dimethylformamide, isopropyl alcohol, methyl alcohol, pyridine, formic acid, and acetone. None of these displaced all of the brown material from all of the samples. However, acetone, isopropyl amine and methyl alcohol were among the best and were about equally good. Acetone was selected as the eluent for future work for reasons of convenience.

Sample Size

The ratio of brown zone length to sample volume was not quite constant, and accordingly, it was necessary to standardize on fuel volumes. A sample volume of 0.5 ml was convenient for gummy fuels giving a zone length in mm approximately equal to gum content in mg/dl. A sample volume of 2.0 ml was used for fuels containing less than about 30 mg/dl in order to assure a long enough brown zone for accurate measurement.

Flow Rate

The brown zone became longer and more diffuse as the pressure and flow rate were increased. It was found that pressures of up to 10 psi could be employed when the brown zone was in the upper part of the column, but that when it reached the lower part, where readings are taken, the pressure should be decreased to between 0 and 5 psi because the zones then become sharper.

Inhibitors

Ionol^{a)} and Tenamine-1^{b)} in abnormally high concentration (0.03% or 10 lbs/5000 gal) showed little effect on the brown zone obtained with an aged thermally cracked jet fuel. With the same amount of UOP-5^{c)} there was a 10-15% increase in gum zone length. It is concluded that the inhibitors in practical concentrations (1 lb/5000 gal) would not affect the results significantly.

Adsorbents and Sample Composition

The relatively long, brown zones obtained on Grade 923 silica gel with samples containing at most only a fraction of a per cent of gum may be explained on two bases. 1) The gum molecules are too large to enter

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- a) 2,6-Di-tert-butyl-4-methyl phenol.
 - b) N,n-butyl-p-amino phenol.
 - c) N,N'-di-sec-butyl-p-phenylene diamine.

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the pores of the adsorbent (32 A average pore diameter). 2) The gum forms an adsorption azeotrope or "asorbotrope" (a mixture which is not separated by passage over the silica gel) with the sample aromatics. The asorbotrope contains only a small concentration of gum and hence the apparent gum zone is long. These hypotheses have been studied and both of them seem to have some merit.

Several adsorbents with larger pores than the Grade 923 silica were employed for gum separation, including Grade 70 silica gel (100 A), alumina (40 A), and silicic acid (50-100 A). In all cases the gum was much more strongly adsorbed and in a shorter zone than on Grade 923; in fact the gum often could not be displaced by any available eluent. Adsorbents of smaller pore size were not studied. Grade 923 gel appears to be suitable and it has the advantage of being available in most of the laboratories where hydrocarbon type analyses are carried out (see the FIA method, SMS 644/52).

Fuel composition also affects the length of the brown zone. For example, when benzene was added to certain jet fuels or gas oils the zone became much shorter. Gasoline gum zones are also very short, due perhaps to the presence of high concentrations of benzene. These observations suggested that an asorbotrope of gum with aromatics (which, like the gum, are adjacent to the eluent front), is formed. Apparently the length of the brown zone depends on the concentration of gum in the asorbotrope, which in turn depends on the nature of the aromatics present. Hence a search was made for a single component solvent that would displace the multicomponent, unpredictable aromatics.

Asorbotroping Solvents

In order to be suitable for chromatographic gum determination the solvent must meet two adsorbability requirements. It must displace the sample aromatics, but not the gum. Thus both solvent and gum would appear as an asorbotrope just below the eluent front. In addition the solvent must form a reasonably long brown zone for a given gum content.

It was found that anisole, ethylene dichloride, isopropyl chloride and α -methyl-naphthalene (MN) are in the right adsorbability range. Of these MN forms the longest brown zones and hence provides the greatest precision. Isopropyl chloride is almost as good, but more sample is required to produce a given brown zone length. Enough MN (0.3-0.4 ml) was employed to contain all the gum. The MN reduced the very long gum zones obtained with certain gas oils and increased the zones obtained with gasolines, but had little effect on jet fuels. Thus all the fuels were put on a common chromatographic basis. Since the composition of jet fuel is not rigidly specified, it is considered preferable to employ the solvent for this as well as other types of fuel.

Dilution of Benzene-Free Fuels

When 2.0 ml samples of gas oil were employed without dilution the flow through the column at 10 psi was slow, and 5 or 6 hours were required for the analysis. In addition, the gum zones were very long with this amount of sample. Dilution of the sample with 50-75% of its volume of benzene reduces the time of analysis to 2 or 3 hours and shortens the brown zone. The benzene diluent is displaced by the MN which is added after the sample. Benzene dilution also affected the separation of 0.50 ml gas oil samples, though not as much. In the absence of data on other benzene-free fuels (for example, diesel fuel or gasoline saturates) dilution is recommended for such materials.

Summary of the Chromatographic Method

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 α -methyl-naphthalene and then acetone eluent. The length of a brown zone containing the gum is measured and empirically correlated with the steam-jet gum content.

The complete procedure is given in EMS 6M2/54 in the Appendix.

Discussion of Results on Jet Fuels and Gas Oils

The jet fuels discussed here represent straight run, thermally cracked, catalytically cracked and blended samples from various sources. This is considered to be a good cross-section of emergency type JP-4 jet fuels. The gas oils are all distillation fractions from a catalytically cracked stock having a 90% end point of 585°F (310°C). It is believed that other gas oils of similar end point would behave about the same.

The brown zone length for jet fuels and gas oils of known steam-jet (500°F) gum content was determined with 0.5-ml samples, and the data are plotted in Figure 1. At gum values above ca 30 mg/dl the data deviate some 10% on the average from the line drawn on the figure. This agreement is considered adequate.

At steam-jet gum values below ca 30 the chromatographic data diverge more seriously from the curve, particularly in the case of gas oils. These low gum fuels were chromatographed using 2.0 ml samples, and the data are shown in Figure 2, together with some gasoline results that are discussed below. It will be observed that there are two clusters of gas oil points in the 30-40 mm region (encircled in the graph). These represent sets of steam-jet values obtained on different occasions (most of the lower values were found later and hence the effect is not due to interim aging). The shape of the lower part of the curve can be determined with more certainty when more comparative data are available.

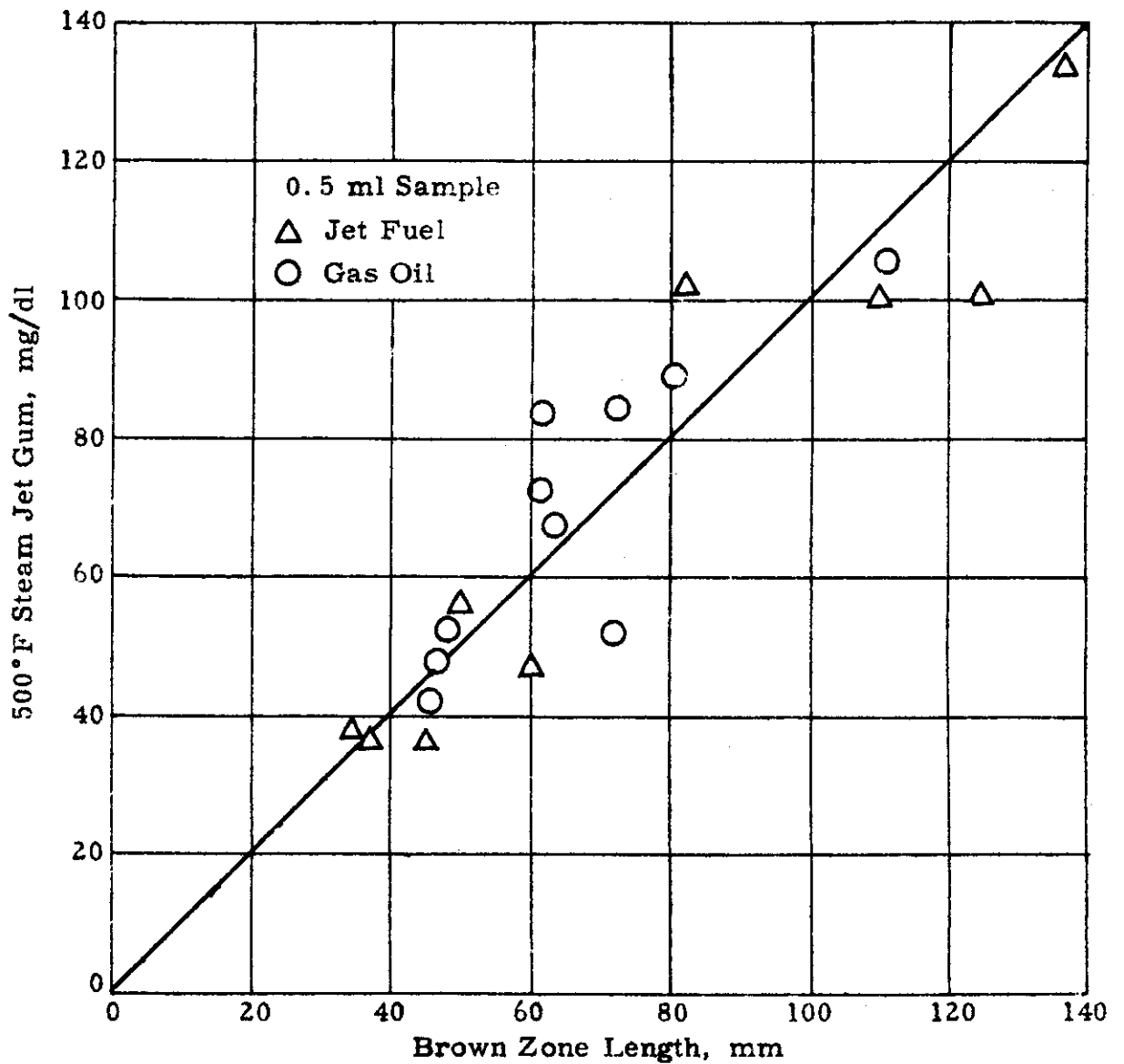


Figure 1. STEAM JET GUM AND CHROMATOGRAPHIC BROWN ZONE

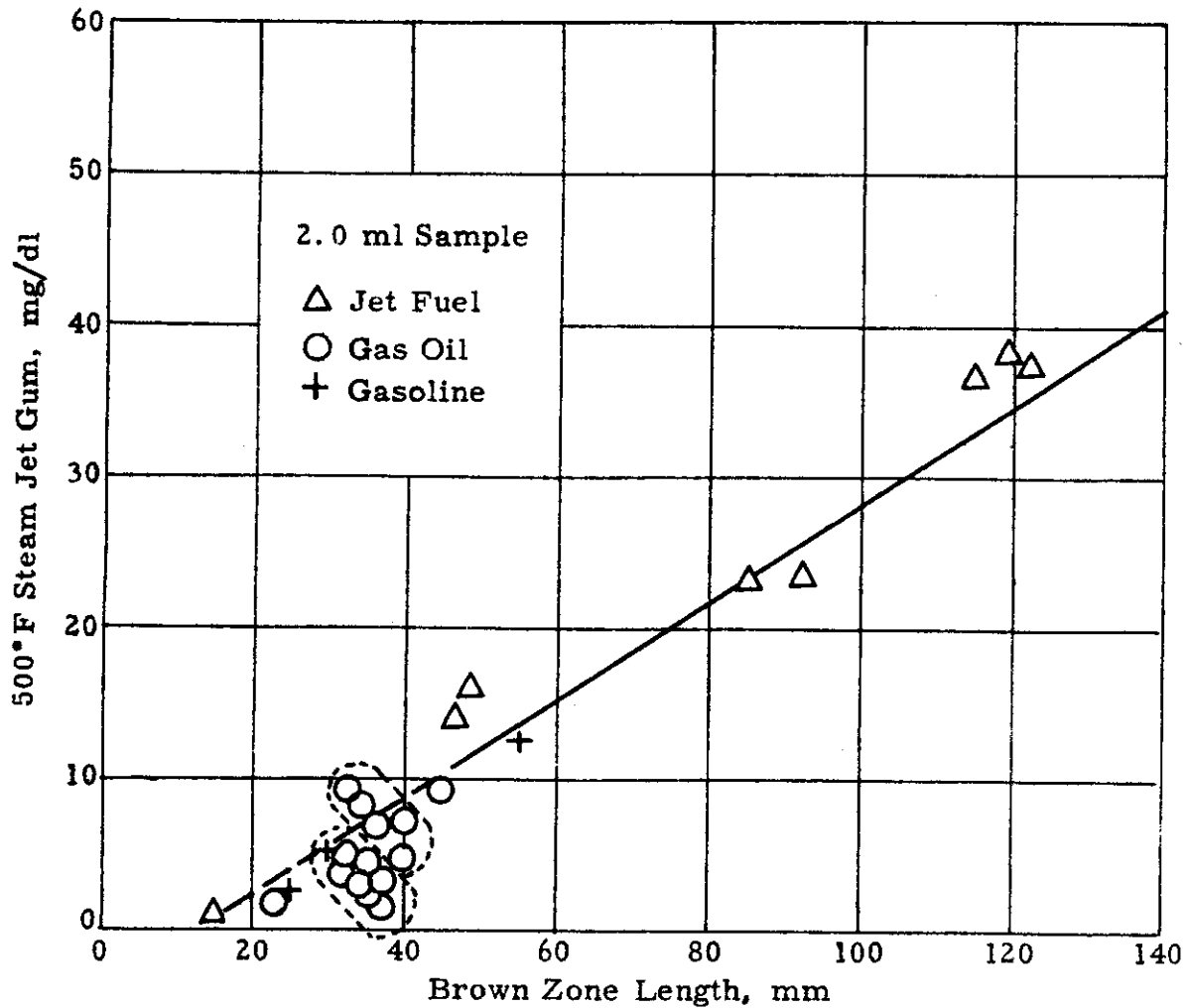


Figure 2. STEAM JET GUM AND CHROMATOGRAPHIC BROWN ZONE - LOW GUM CONTENT

Discussion of Results on Gasoline

Preliminary tests on three gasolines of moderate gum content, as determined by the steam-jet method at 500°F, showed that there is a correlation between gum content and zone length also for this type of fuel. The data are included in Figure 2. So far no correlation has been observed between the chromatographic gum and gum determined by the air-jet procedure at 330°F (ASTM D-381). However, this may be due to the formation of gum during the air-jet evaporation, which is known to occur with some gasolines.

Evaluation of the Proposed Method

A study of a group of gas oils was carried out in which the steam-jet and chromatographic gums were determined in duplicate in a randomized sequence (the duplicates were not run side by side, in general). The standard deviations for repeatability of the steam-jet and chromatographic methods were 7 and 10%, respectively. The chromatographic method has since been improved by specifying that the reading be taken when the brown zone is fairly high in the analyzer, and it is believed that the precisions of the two methods are now about equal.

The chromatographic method gives values that are probably acceptably close to those obtained by the steam-jet method for jet fuels and some gas oils. It also shows promise of correlating with the steam-jet method for gasolines. It requires only 0.5 to 2.0 ml of sample, the equipment and procedure are simple, and one operator with facilities for 10 columns can make 15-30 determinations in 8 hours.

Outline of Future Work

More work will be done with gas oils from various sources to verify the applicability of the new method to this type of fuel. It may also be possible to determine the oxidation products in lube oils by this or a related procedure. Determination of the low gum content (less than 5 mg/dl) in commercial products is important and therefore data on all types of such clean fuels are desirable.

Although this report is concerned with soluble gum, the importance of developing a method for insoluble gum has not been overlooked. Experiments are in progress covering methods of recovery and determination of gum suspended in the fuel or deposited on the walls of the container.

The relation between gum zone length and steam-jet gum is presently obtained from a large number of determinations by both methods. Development of a standardized oxygenated polymer for calibration of adsorption gum equipment could eliminate such extensive testing, and would serve as a standard between laboratories, different adsorbent supplies, etc.

SHELL DEVELOPMENT COMPANY
ANALYTICAL DEPARTMENT¹⁾

Determination of

SOLUBLE GUM IN FUELS
CHROMATOGRAPHIC METHOD

SCOPE

1. This method describes a procedure for the determination of soluble gum in jet fuels and similar petroleum distillates boiling up to about 310°C (585°F). The gum values correspond to those obtained by a steam-jet evaporation procedure (SMS 178, but 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 α -methyl-naphthalene and then acetone 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 and meter rules adjacent to the Analyzers makes a convenient arrangement. (See Figure 1, SMS 644/52)

(b) Hypodermic Tubing, No. 19 Stubs gage, about 90 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+%.

1) This method represents current opinion as of the date of issue, but may be revised from time to time. Questions regarding application of the method should be directed to Analytical Department, Shell Development Company, Emeryville, California

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(c) α -Methylnaphthalene, Eastman practical grade, decolorized over silica gel.

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

PROCEDURE

5. (a) Attach the tip containing a cotton plug, and fill the column with silica gel, applying the rubber-padded vibrator as needed, until the packed gel level is 5 to 10 mm below the top of the Separator section.

(b) Introduce the sample, as follows:

1) If the gum content is above ca 30 mg/dl use 0.50 ± 0.03 ml, otherwise use 2.00 ± 0.05 ml.

2) If the benzene content of the sample is not known to exceed 10%, mix two volumes of sample with one volume of benzene, and use 3.00 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 followed as rapidly as possible by the sample.

(c) Apply a pressure of 5 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 sample. When the sample is taken up, add 0.3 to 0.4 ml α -methylnaphthalene and apply pressure as above. After this is absorbed rinse the walls of the column with a few drops of acetone and force this into the adsorbent. Then fill the Charger with acetone and apply pressure as above until the top of the brown zone reaches the top of the Analyzer. Reduce the pressure to 5 psi for gas oils or 1 psi for jet fuels and gasolines.

(d) After the brown zone has progressed an additional 100 to 150 mm, 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 50 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.

Note 2. α -Methylnaphthalene is a primary skin irritant and must therefore be handled with care. It will be necessary to provide some means of collecting the effluent from the column, and it may be desirable to reapply the pressure and force the hydrocarbon and gum out of the column altogether before cleaning.

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CALCULATION

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

(a) For 0.5 ml sample,

$$\text{Gum, mg/dl} = \text{Zone length, mm}$$

(b) For 2.00 ml sample,

$$\text{Gum, mg/dl} = 0.33 \times \text{Zone length, mm} - 5$$

PRECISION

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

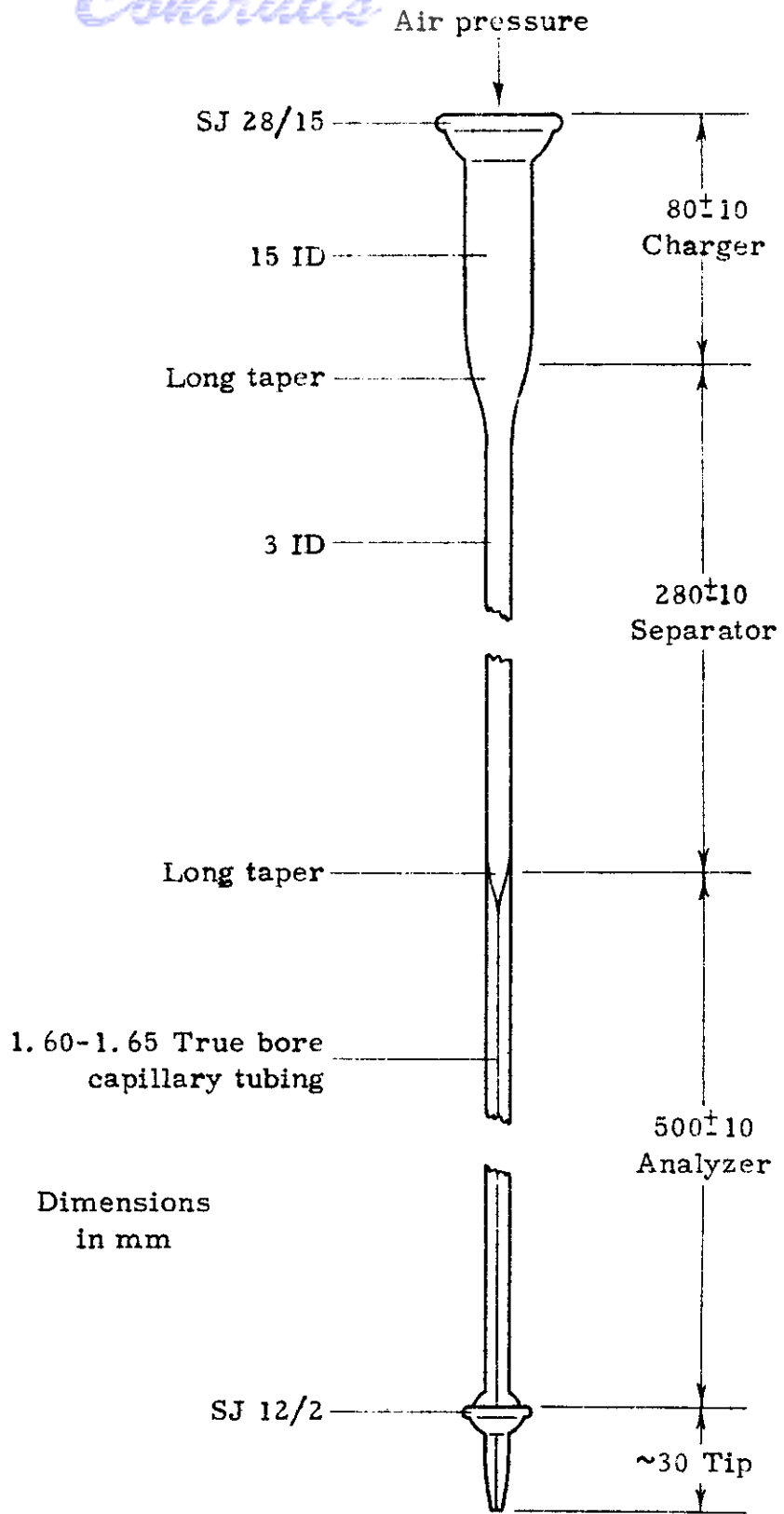


Figure 1. ADSORPTION COLUMN