SECTION I

PURIFICATION OF SOLVENTS FOR THE ULTRAVIOLET SPECTROPHOTOMETRY
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INTRODUCTION

Many Organic compounds have been used as solvents in ultraviolet spectrophotometry. The more common polar solvents are water, methanol and ethyl alcohol, while the nonpolar solvents often used are n hexane, cyclohexane and 2, 2, 4 trimethyl pentane (isooctane).

The commercial samples of these liquids contain traces of impurities, which absorb ultraviolet light, thus decreasing their transmission in this part of the spectrum, particularly at lower wavelengths.

PREVIOUS WORK

The process of purification of these and other solvents have been described by several workers.

Hydrocarbon Solvents

Castille and Henri described a process for the purification of a fraction of petroleum ether containing mainly hexane. Petroleum ether was shaken with fuming sulfuric acid for twelve
hours, separated and washed with distilled water, it was then shaken for twelve hours every time, firstly with 300 ml. of 10% sodium hydroxide, secondly with a mixture of 200 ml. of 5% potassium permanganate and 100 ml. of 10% sodium hydroxide, and thirdly with a mixture of 200 ml. of 5% potassium permanganate and 100 ml. of 10% sulfuric acid, washed with water, dried and distilled.

Adsorption methods for the purification of solvents for absorption spectrophotometry using silica gel as adsorbent have been suggested by Mair and Foziarty, by Graff, O'Connor and Steau, Ashmore, Potts and by Vinogradov.

Hexane was purified by Pirlot by distillation, and passing the distillate over a column of activated charcoal.

Linne and Umar purified cyclohexane by refluxing it with fuming sulfuric acid for six hours, cooling and washing it respectively with dilute sodium hydroxide solution and water. Kubo purified cyclohexane by shaking it with activated carbon for two hours.

Hesse and Schildmecht have compared various methods for the purification of hydrocarbon solvents for ultraviolet spectroscopy.

Alcohol Solvents
After comparing several methods for the purification of ethyl
alcohol, Leighton, Crary, and Schipp\textsuperscript{11} suggest for the best results the following method. Ethyl alcohol was to be refluxed with 10 ml. of 12 N sulfuric acid for twelve hours and distilled. The distillate was then to be refluxed with the addition of 20 gms/liter potassium hydroxide and 10 gms/liter of silver nitrate and again distilled. The distillate is afterwards dried over aluminum amalgam.

Clow and Pearson\textsuperscript{12}'s method for the purification of ethyl alcohol for absorption spectrophotometry consists in refluxing it with 4 c.c./liter of concentrated sulfuric acid for two hours and subsequently distilling, the first and the last ten per cent portions being rejected. The middle fraction is treated with 1.5 gms/liter silver nitrate and 3 gms potassium hydroxide/liter stirred, filtered and distilled. Finally, the middle fraction of the second distillation is distilled over calcium oxide in an atmosphere of nitrogen.

Purification of ethyl alcohol by distillation, either over activated charcoal (Pirlot, loc. cit) or over phosphorous pentoxide, and refluxing with potassium hydroxide prior to final distillation (Gage and Wender\textsuperscript{13}) have also been reported.
EXPERIMENTAL

(A) Hydrocarbon Solvents

(i) n hexane

Hexane (B.D.H), the fraction of petroleum boiling between 67° - 70° was used. It was purified by the methods of Castille and Henri (loc. cit) (Curve A, fig.1), as well as by passing it over the columns of (i) silica gel (Mair, et al; loc. cit, Graff et al. loc. cit) (Curve B, fig. 1), (ii) activated charcoal (Pirlot, loc. cit) (Curve C, fig. 1), and (iii) first over a column of silica gel and then over a column of aluminium oxide (Hesse and Schildknecht, loc. cit) (Curve D, fig. 1).

According to another method adopted, a preliminary purification of hexane was carried out by stirring it with a mixture of sulfuric acid and nitric acid at 0° C, for four hours, separating and washing with distilled water, and distilling. The distillate was dried over 'drierite' (anhydrous calcium sulfate) and passed over a 100 c.m, column of silica gel and subsequently over a 50 c.m, column of aluminium oxide, (Curve E, fig.1).

It will be observed from fig. 1 that the last process yields hexane which is most transparent in the ultraviolet region.

(ii) Cyclohexane

Cyclohexane (B.D.H) was purified by treatment with (i) activated charcoal (Pirlot, loc. cit; Kubo, loc. cit) (Curve A, fig.2),
(ii) Silica gel (Pirlot loc. cit) (Curve B, fig. 2).
(iii) Silica gel and subsequent treatment with aluminium oxide
(Hesse, Schildknecht, loc. cit) (Curve C, fig. 2). It was also purified by the method of Linnel and Umar (loc. cit)
(Curve D, fig 2).

In another process, a preliminary purification of cyclohexane was carried out by treatment with sulfuric acid, washing with water, drying with drierite and finally distilling. The distillate was then passed over a 100 cm² column of silica gel and over a 50 cm² column of aluminium oxide (Curve E, fig. 2). This last process gives the most transparent solvent.

(iii) n heptane
A preliminary purification of n heptane (Riedel) was carried out by stirring it with concentrated sulfuric acid for twelve hours. After separating it from sulfuric acid, it was washed twice with distilled water, dried over drierite and distilled. The distillate was passed over a 100 cm² column of silica gel and a 50 cm² column of aluminium oxide (Curve A, fig. 3).

(iv) Methyl cyclohexane
Methylcyclohexane (L. Light) was similarly purified by stirring it with a mixture of concentrated sulfuric acid and concentrated nitric acid at 0° C for four hours. It was then separated, washed twice with distilled water, dried over drierite, and
distilled. The distillate was passed over a 100 cm$^3$ column of silica gel and a 50 cm$^3$ column of aluminium oxide (Curve B, fig. 3).

(B) Alcohol Solvents

(i) Methanol

A sample of B.D.H. methanol was purified by distillation and passing the distillate over a column of activated charcoal (Pirlot, loc. cit) (Curve A, fig. 4). In another case, the methanol was refluxed with 10 gms/liter sodium hydroxide and 10 gms/liter silver nitrate for twelve hours and distilled. The distillate was dried over drierite and finally redistilled (Curve B, fig. 4).

(ii) Ethyl Alcohol

Commercial ethyl alcohol made in the Government sponsored distillery, Baroda, was used for purification according to methods of

(i) Leighton et. al. (loc. cit) (Curve A, fig. 5), (ii) Pirlot (loc. cit) (Curve B, fig. 5), (iii) Gage and Wender (loc. cit) (Curve C, fig. 5). It will be observed from the results that the best sample is obtained by the method of purification adopted by Leighton et. al.

(iii) Isopropyl alcohol

The sample of isopropyl alcohol (B.D.H) was refluxed with 5 gms/liter silver nitrate and 10 gms/liter potassium hydroxide for twelve hours and distilled; the distillate was dried over drierite and redistilled (fig. 6).
Figure 1 - Transmission of ultraviolet light by n-Hexane.

A - purified by method of Castille and Henry.
B - purified by passing over silicagel.
C - purified by passing over activated charcoal.
D - purified by method of Hesse and Schildknecht.
E - purified by process described on page 15.
F - untreated.

Figure 2 - Transmission of ultraviolet light by Cyclohexane.

A - purified by passing over activated charcoal.
B - purified by passing over Silicagel.
C - purified by the method of Hesse and Schildknecht.
D - purified by the method of Linnel and Umar.
E - purified by process described on page 16.
F - untreated.
Figure 3 - Transmission of ultraviolet light by:

- A - pure n-Heptane,
- B - pure methylcyclohexane,
- C - Untreated n-Heptane,
- D - Untreated methylcyclohexane.

Figure 4 - Transmission of ultraviolet light by:

- A - Methanol purified by method of Pirlo,
- B - Methanol purified by the process described,
- C - Untreated methanol.
Figure 1. Transmission of ultraviolet light by
isopropyl alcohol.

1 - purified by method of Jennings et al.
2 - purified by action of Cuprammonium
3 - untreated.

Figure 4. Transmission of ultraviolet light
by isopropl alcohol.

A - purified by process outlined on
page 17
B - Untreated.
REFERENCES


