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# ULTRAVIOLET AND INFRARED SPECTROPHOTOMETRIC ANALYSIS OF AN INSECT REPELLENT MIXTURE

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## Abstract

A spectrophotometric procedure employing measurements in both the ultraviolet and infrared regions was developed to determine the concentrations of N-butyl acetanilide, benzyl benzoate, 2-ethyl, 2-butyl propanediol-1,3 and Tween 80, in a mixture containing only these four components.

The first two components have relatively strong absorptivities in the ultraviolet at 227.5 and 280.3 millimicrons, while the latter two have absorption bands at the infrared wavelengths, 8.99 and 9.60 microns. By substituting the absorptivities at these wavelengths in a set of four simultaneous equations, the percentage of each component in an insect repellent mixture is calculated.

## Introduction

Numerous analytical procedures are found in current literature for quantitative determination of one or more components in a sample by means of absorption spectrophotometry. Generally the methods are restricted to absorption of radiation in one spectrum, e. g., ultraviolet, visible, infra red, microwave, or X-radiation. However, where instruments are available for utilization of more than one of these spectra, an analysis may be simplified by selecting wavelengths in two or more regions at which absorbance occurs by components of the sample.

Concentrate M 1960 procured by the Armed Forces is so formulated that the three active components N-butyl acetanilide, benzyl benzoate and 2-ethyl, 2-butyl propanediol-1, 3 together with a wetting and emulsifying agent Tween 80\* are present in the approximate proportions 3:3:3:1 respectively. Although other methods of analysis (1, 2) have been developed for this composition, the procedure presented here is considered most suitable because all four components are determined directly, by utilizing absorbance measurements in the ultraviolet and the infrared regions and because the spectra of the individual materials give a qualitative indication of their purity as compared with standards.

\*Polyoxyethylene sorbitan mono-oleate

## Experimental

### Reagents:

95% ethanol: a large enough lot to complete an entire analysis, to prevent possible differences due to solvent.

CCl<sub>4</sub>: redistilled, sufficient to complete entire analysis

N-butyl acetanilide

Benzyl benzoate

2-ethyl, 2-butyl propanediol-1,3

Tween 80

The last four (components) are to be taken from the same lots used in the composition of the M 1960 mixture under test.

### Apparatus:

Beckman DU ultraviolet spectrophotometer (or equivalent)

1 cm quartz cells.

Beckman IR-2 infrared spectrophotometer (or equivalent)

0.1 mm NaCl cells.

### Procedure

#### A. Ultraviolet Section

1. The following materials are weighed, each into a separate 100 ml. volumetric flask.

N-butyl acetanilide (A) 1.5 ± 0.5000 grams

Benzyl benzoate (B) 1.5 ± 0.5000 grams

2-ethyl, 2-butyl 1.5 ± 0.5000 grams

propanediol-1,3 (D)

Tween 80 (T) 0.5 ± 0.1000 grams

Sample (S) 5.0 ± 1.0000 grams

2. Each material is diluted to the mark with 95 percent ethanol and shaken well to assure complete solution. (These are stock solutions for use in the ultraviolet region only).

3. A set of dilute solutions is prepared from the stock solutions (Step 2) by transferring 1.0 ml. of each to separate 100 ml. volumetric flasks, then diluting to the mark with 95 percent ethanol. To obtain homogeneity, the solutions are thoroughly agitated.

4. A second set of dilute solutions are prepared from those in Step 3 by pipetting 5 ml. of each into separate 100 ml. volumetric flasks and diluting with 95 percent ethanol.

5. Using the spectrophotometer, absorbances of the series from Step 3 are obtained at 280.3 m $\mu$  and of the series from Step 4 at 227.5 m $\mu$ . The slit width is kept the same for each particular wave length throughout each series and 95 percent ethanol is used in the comparison cell.

#### B. Infrared Section

6. From the same lot of materials used in Step 1 the amounts shown below are weighed into separate 100 ml. volumetric flasks.

N-butyl acetanilide (A)	3 $\pm$ 0.5000 grams
Benzyl benzoate (B)	3 $\pm$ 0.5000 grams
2-ethyl, 2-butyl propanediol-1, 3 (D)	3 $\pm$ 0.5000 grams
Tween 80 (T)	1 $\pm$ 0.1000 grams
Sample (S)	10 $\pm$ 1.0000 grams

7. The material in each flask is diluted with redistilled carbon tetrachloride and agitated thoroughly to assure complete solution.

8. 25 ml. of each of the above solutions (Step 7) is transferred to separate 100 ml. volumetric flasks and diluted to the mark with redistilled carbon tetrachloride. The solution is agitated thoroughly.

9. Absorbances of the series from Step 7 are obtained at 9.60 microns and of the series from Step 8 at 8.99 microns on the infrared spectrophotometer. The slit width is again kept constant for each particular wavelength throughout each series and redistilled carbon tetrachloride is used for comparison.

### Calculations and Results

Absorptivities are calculated for each solution from the absorbances, exact concentrations, optical path, and corrections for cell differences by using the equation:

$$a_{(n,j)} = \frac{A'_{(n,j)}}{C'_n b} \quad 1.$$

- Where a = absorptivity of the solution  
 A' = absorbance of solution  
 C' = concentration of solution  
 b = optical path through solution  
 n = particular solution (component or mixture)  
 j = wavelength at which absorbance was read

The values of "a" found by equation 1. are introduced into the four simultaneous equations 2. which are then solved for the fractions C<sub>n</sub> of the components in the mixture.

$$a_{(s,j)} = \sum_n a_{(n,j)} C_n \quad 2.$$

- Where s = sample  
 j = 227.5 millimicrons, 280.3 millimicrons,  
 8.99 microns, 9.60 microns

An alternate calculation can be used in this case since the absorptivities  $a_{(D,227.5)}$ ,  $a_{(T,227.5)}$ ,  $a_{(D,280.3)}$  and  $a_{(T,280.3)}$

will generally be so small as to be negligible. The first two equations from 2. above can then be written

$$a_{(S,227.5)} = a_{(A,227.5)}C_A + a_{(B,227.5)}C_B \quad 3.$$

$$a_{(S,280.3)} = a_{(A,280.3)}C_A + a_{(B,280.3)}C_B \quad 4.$$

These equations may then be solved for C<sub>A</sub> and C<sub>B</sub> and the values inserted in the last two equations from 2. which can in turn be solved simultaneously for C<sub>D</sub> and C<sub>T</sub>. The fractions C<sub>n</sub> are multiplied by 100 to convert to percent.

The analyses of three concentrate mixtures, by the method outlined, give results as shown in Table I. The results in column (2) were obtained by the alternate method of calculation mentioned above. Mixtures 1 and 2 were dissolved in absolute ethanol but the results indicate no effects, although greater care in handling was necessary during analysis.

### Discussion

Two wavelengths — 227.5 and 280.3 millimicrons — were selected from the curves shown in Figure 1 as char-

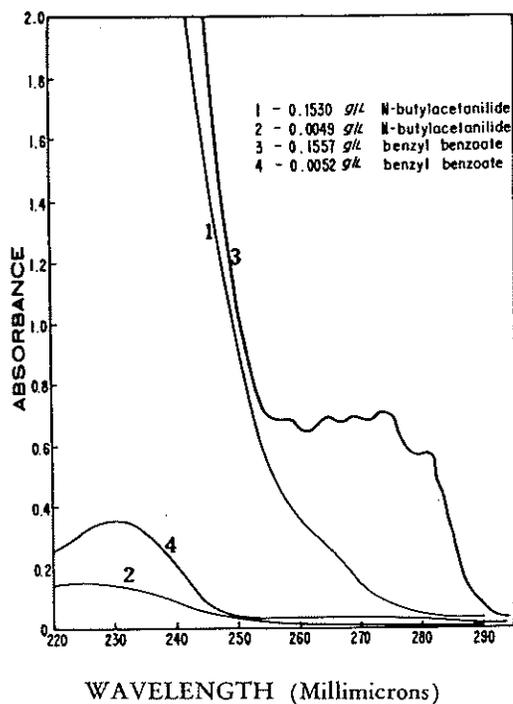


Fig. 1. Ultraviolet absorption spectra of 95 percent ethanol solutions of two redistilled components in M-1960.

acteristic absorption bands for the two compounds — benzyl benzoate and N-butyl acetanilide. Since only slight absorption in the ultraviolet range was shown by 2-ethyl, 2-butyl propanediol-1, 3 and Tween 80; all four components and an M 1960 mixture were examined under infrared radiation resulting in the curves shown in Figure 2. As expected all the components have numerous characteristic infrared absorption bands which are well defined. One might be led to believe that the infrared data alone would be sufficient for the analysis. However, when absorbances were determined for the components and mix-

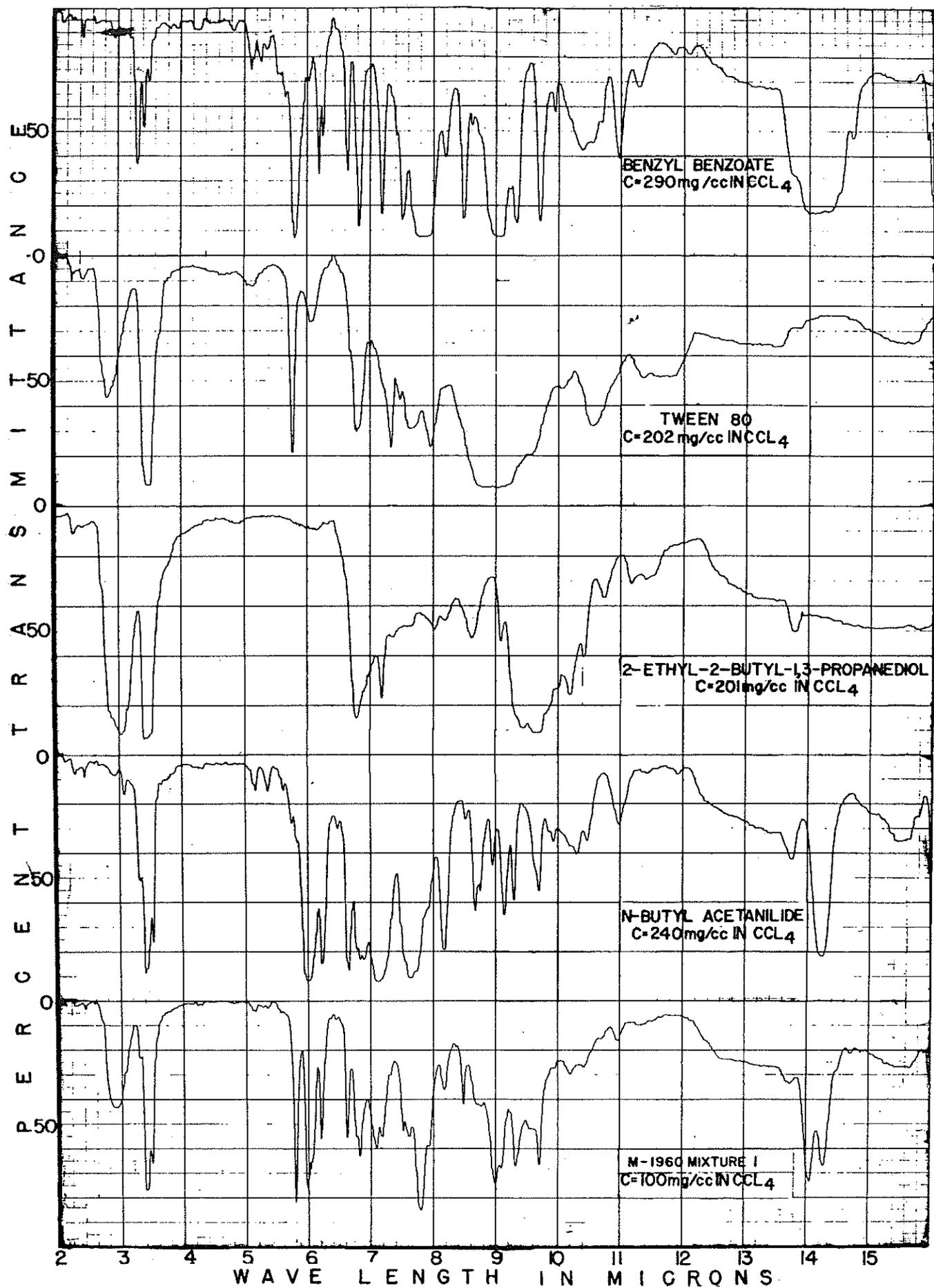


Fig. 2: Infrared spectra of CCl<sub>4</sub> solutions of the components and mixture 1 of insect repellent M-1960.

TABLE I  
RESULTS OF THE PROPOSED  
METHOD OF ANALYSIS

Mixture Analyzed	Component in Mixture	Percentage Concentration		
		Known	Calculated (1) *	Calculated (2)
1	A	29.5	24.9	25.8
	B	31.1	31.0	31.4
	D	29.5	31.4	31.3
	T	9.9	9.9	9.4
2	A	29.7	26.0	28.6
	B	29.5	29.8	30.2
	D	29.8	31.9	31.8
	T	11.0	10.5	10.0
3	A	30.0	35.7	32.8
	B	30.0	28.8	30.5
	D	30.0	32.4	33.1
	T	10.0	9.9	8.8

\* (1) Calculated from four simultaneous equations taking all absorptivities into account.

ture at the characteristic wavelengths, many bands were found to be unusable because they interfered with others. It was therefore decided to use characteristic spectra in the ultraviolet for two of the components and absorption bands in the infrared at 8.99 and 9.60 microns for 2-ethyl, 2-butyl propanediol-1, 3 and Tween 80 respectively. Determination of the four components by absorption spectroscopy utilizing two spectral regions, viz., ultraviolet and infrared is an advantage over the other methods (1, 2) developed concurrently in other laboratories.

Also considered in this investigation was the usual deviation from the Beer-Bouguer law due to large variations in concentration. This is indicated in Table II giving absorptivities vs concentration for N-butylacetanilide in 95% ethanol solutions. Absorptivities obtained over a narrow range of concentration, however, vary no more than those obtained on a single solution. To avoid errors due to concentration variations, the solutions of each component, alone and in mixtures were prepared at about the same concentration.

Furthermore, since the materials used in the mixture may contain minor impurities of a not too constant nature, absorptivities were obtained on the same materials used in the formulation. This is considered necessary until a study can be made of the nature and amounts of impurities in the components with attendant effects on absorptivities.

The results on the three samples shown in Table I were obtained by choosing the proper solution concentrations and by obtaining the absorptivities on the same lot

TABLE II  
DEVIATIONS OF COMPONENT "A"  
FROM BEER-BOUGUER'S LAW

Conc. g/l	Absorptivities	
	227.5 m $\mu$	280.3 m $\mu$
0.4	—	0.09
0.3	—	0.10
0.2	—	0.12
0.1	—	0.14
0.02	27.9	—
0.01	29.1	—
0.005	32.9	—

of components used in a particular mixture. Comparison of the calculated results with the known values shows an average deviation of 1% or less for three of the components but N-butyl acetanilide has a somewhat greater deviation. No explanation has been found for this since several experiments using purified N-butyl acetanilide gave no better accuracy. It is believed, however, that the cause is inherent in the mixture and may not be encountered in mixtures of other substances to be analyzed by this method.

In this particular case greater accuracy has not been stressed because the efficiency of the repellent mixture is not appreciably effected by a variation of several per cent in a component (2). Greater emphasis has been placed upon the application of a procedure which allows the use of different instruments and techniques for measuring absorption of radiations at widely separated wavelengths. This may not necessarily be limited to the ultraviolet and infrared regions.

### Conclusions

A method has been developed for the simultaneous determination of the four components: N-butyl acetanilide, benzyl benzoate, 2-ethyl, 2-butyl propanediol-1, 3 and Tween 80, in insect repellent concentrate M 1960 by the combined use of absorbances obtained at selected wavelengths in the ultraviolet and infrared regions.

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### Literature Cited

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