

Fig. 4. Co-oxidation of glucose present in methyl linoleate-glucose system, initial concn 6.31×10^{-4} mole glucose/mole linoleate, 50C, initial pH 7.00.

of linoleate hydroperoxide decomposition into free radicals and on the acceleration of autocatalysis.

The mechanism for linoleate oxidation in the presence of polyhydroxy compounds may be summarized as follows:

(methyl linoleate RH and its hydroperoxide ROOH)

Initiation: $RH + O_2 \rightarrow ROOH$
 $ROOH + \text{Polyhydroxy compounds} \rightarrow ROO'$
 or $R' + \text{oxidation products of polyhydroxy compounds}$

Propagation: $ROO' + RH \rightarrow ROOH + R'$
 $R' + O_2 \rightarrow ROO'$

Chain termination: $ROO' + ROO' \rightarrow \}$
 $R' + ROO' \rightarrow \}$ Inactive products
 $R' + R' \rightarrow \}$

In conclusion, all polyhydroxy compounds tested have shown to accelerate the oxidation of methyl lino-

leate emulsions. The oxidation rate constants of methyl linoleate vary considerably from one polyhydroxy compound to another and can be linked with the functional groups present and the mol wt. Activation energy values for methyl linoleate oxidation in their presence are less than the value for autoxidation, 18.20 K cal/mole (18).

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• Letters to the Editor

Infrared Determination of Alkyl Branching in Detergent ABS

IN DETERMINING the level of alkyl benzene sulfonate (ABS) in sewage by the Soap and Detergent Association (SDA) method (1), we have found that the relative amounts of straight and branched chain isomers can be estimated from the intensities of the 1367 cm^{-1} and 1410 cm^{-1} IR absorption bands. The 1367 cm^{-1} band arises from the methyl deformation vibrations of a number of branched structures present in tetrapropylene ABS. The origin of the 1410 cm^{-1} band has not been established; however, it is associated with the sulfonate group. Its position is dependent upon the nature of the alkyl group, occurring at 1410 cm^{-1} in straight chain isomers and at 1400 cm^{-1} in tetrapropylene-ABS.

ABS is isolated by the SDA method as the 1-methyl heptyl amine salt, then converted to the *n*-octyl amine salt and its absorption between 1450 and 1350 cm^{-1} recorded as a 2-3% solution in CCl_4 . The absorbance ratio of the $1367/1410 \text{ cm}^{-1}$ bands is calculated and the relative amounts of straight and branched chain ABS read from a calibration curve. The octyl amine salt is used rather than the 1-methyl heptyl amine because it avoids an additional methyl branch absorption in the analytical region. Calibration standards

are 1) a 99+% pure straight chain sodium ABS (mol wt 348) composed of a mixture of 2,3,4,5, and 6 phenyl isomers, and 2) the SDA standard tetrapropylene ABS. These materials most nearly approximate commercial ABS. Typical IR curves show in Figure 1 and 2.

Method

Reagents. Basic Solution—15 g NaCl, 40 ml 3A alcohol, 25 ml 0.5 N NaOH and 3 ml 0.1% chlorophenol red indicator solution into a 500 ml volumetric flask. Fill to volume with distilled water and mix well.

Phosphate buffer, pH 6.8

Petroleum ether (PE), redistilled

Calibration. Convert the sodium ABS calibration standards to their *n*-octyl amine salts by the procedure described in the SDA method. Prepare a series of mixtures ranging from 5-95% of each standard and dissolve in CCl_4 to make 2% solutions on the sodium ABS basis. Scan the $1450-1350 \text{ cm}^{-1}$ spectral region in a 1-mm cell vs. a CCl_4 blank, using a five-fold expansion of the wavelength scale. Measure

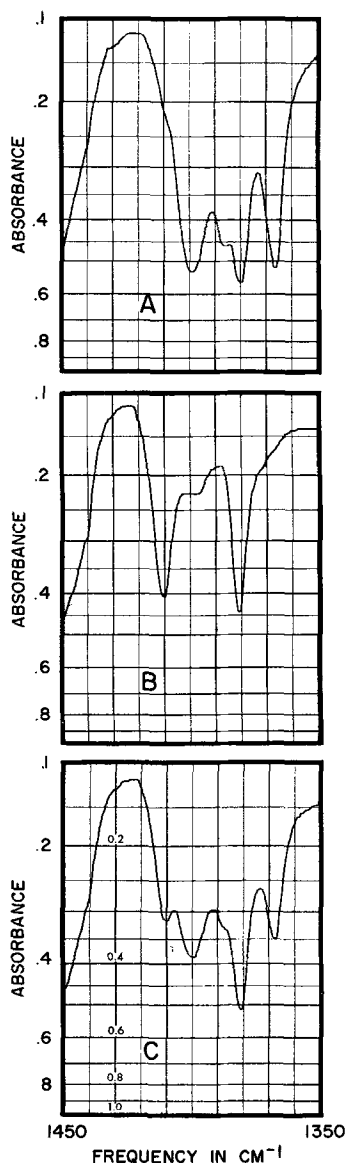


FIG. 1. Spectra of calibration standards.

- A. 100% tetrapropylene ABS.
 B. 100% straight chain ABS.
 C. 50/50 mixture of A & B.

the absorbance of the analytical peaks, subtracting the background absorbance as shown in Figure 2. Prepare a calibration curve plotting the absorbance ratio $1367\text{ cm}^{-1}/1410\text{ cm}^{-1}$ vs. the concn ratio of the mixture.

Procedure. Transfer the CCl_4 solution of the methyl heptyl amine-ABS complex to a 50 ml extraction cylinder and remove the CCl_4 by evaporating with a stream of nitrogen. Add 20 ml "basic solution" and extract three times with 25 ml PE. Shake the cylinder vigorously to insure all ABS is held in the aqueous layer. Discard the PE layers. Neutralize the aqueous layer to the chlorophenol red end point with 0.5 N HCl. Add 10 ml buffer solution and 2 drops *n*-octyl amine. Mix well. Extract three times with successive 20-ml portions PE containing 1 drop *n*-octyl amine. Combine the PE extracts in a 100-ml beaker and evaporate to dryness on a steam bath under nitrogen.

Dissolve the residue in an amount of CCl_4 to make ca. 2% solution on the sodium ABS basis (the amount of CCl_4 required is established from the ppm ABS determined by the SDA method). Scan the spectrum

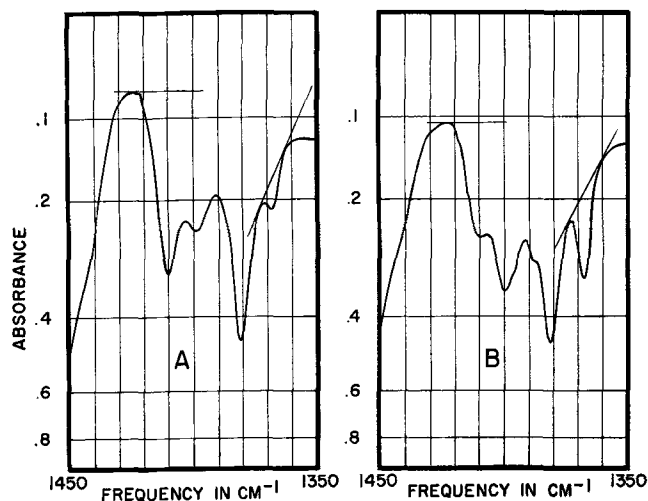


FIG. 2. Spectra of ABS isolated from water.

- A. Sewage disposal plant influent from a controlled test area—analysis, 19% TP-ABS.
 B. Ground water near a cesspool in a test area—analysis, 61% TP-ABS.

of the solution and determine the absorbance ratio of the analytical peaks as described under *Calibration*. Read the relative amounts of straight chain and tetrapropylene ABS from the calibration curve.

Discussion. The IR work was done on a Perkin-Elmer #421 grating spectrometer; however, any of the versatile prism or grating instruments should give comparable results.

The bands in the analytical region are sharp, closely spaced and relatively weak. In order to obtain good accuracy and detection limits, the wavelength scale was expanded five-fold and the solution concn adjusted to give bands of reasonable intensity. Limited data indicate reproducibility of $\pm 2\%$ for most samples. The min detection limit for tetrapropylene ABS is ca. 5%. Accuracy has not been determined experimentally because of the difficulty of reproducing the partially degraded structures present in sewage. It is expected that error will be introduced from the relative difference in mol wt of the straight and branched components and from the possible change in intensity of the 1367 cm^{-1} band for a given amount of partially degraded ABS.

The band ratio technique was selected because of its increased accuracy and adaptability to routine analysis. Since the ABS fraction contains only 10 mg of sample, accurate preparation of solutions of known concn at this level was found not practical on a routine basis.

The purpose of the PE extractions is to 1) further purify ABS, and 2) convert it to the octyl amine salt. The content of carbonyl compounds, nonionic polyether surfactants and brown color bodies is reduced or removed entirely by the extraction.

It is also possible to obtain quantitative results using the much simpler "smear technique" for obtaining the spectra, however, the analytical bands are not as sharp as in solution spectra.

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