# Fast Determination of Fatty Acids in Oil-Utilizing Resins by NMR Spectroscopy

JAROSLAV RYBICKY, *Reichhold Chemicals Limited, Toronto, Ontario, M9M 1B1, Canada*

## Synopsis

This work describes the determination of oil either as such or in oil-utilizing resins such as alkyds and urethanes, by means of NMR techniques. Both the qualitative and quantitative analyses are demonstrated and the accuracy is assessed. Typically, the complete analysis of an alkyd resin takes less than 1 hr.

## INTRODUCTION

The alkyd chemist often faces the task to determine oil in alkyd resins. The present practice is such that a resin is hydrolyzed to its original single components which are then quantitatively determined by gravimetric or volumetric techniques[1,2] and qualitatively identified by gas chromatography.[3–7] The whole process is lengthy and time consuming, and apparently a fast and simple method for the oil determination and alkyd analysis would be appreciated.

Because of the structural similarity of the commonly used oils, spectroscopic techniques have not been extensively employed for the identification of oils despite some early work which indicated the principal potential of nuclear magnetic resonance (NMR) spectroscopy in this respect.[8] In the majority of cases, the NMR spectra are not characterized by the appearance of new peaks when the oil in alkyds is changed. Considering the typical alkyd-utilized oils such as soybean and linseed oils and tall oil fatty acids (TOFA), there is no qualitative difference in the composition of fatty acids of these materials that could give rise to distinct patterns of NMR spectra for the different oils. It is probably for these reasons that gas chromatography remains the only routine method for the identification of oils and fatty acids, despite the tedious prerequisites of the methods.

Under close examination of the typical NMR spectra of oils, however, it can be found that the degree of unsaturation of oils is distinctive enough to provide information on the oil identity. In our laboratory we have successfully identified oils in alkyds by means of NMR spectroscopy. In addition to the identification of oil, the NMR spectra provide the quantitative determination of the oil and the phthalic part, and possibly other components. The procedure is fast and elegant, and it does not require any chemical modification of samples, in contrast to the chromatographic, volumetric, and gravimetric techniques. Typically, the NMR analysis of alkyd solids takes less than 1 hr.

Journal of Applied Polymer Science, Vol. 23, 25–38 (1979)

0021-8995/79/0023-0025$01.00

## THEORETICAL CONSIDERATIONS*

The fatty acids contained in typical alkyd-utilized oils are long-chain organic acids which may have various degrees of unsaturation. For instance, $C_{18}$-fatty acids can have the following structures:

Stearic Acid

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2-CH_2CH_2CH_2CH_2CH_2CH_2COOH$$

Oleic Acid

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH{=}CHCH_2-CH_2CH_2CH_2CH_2CH_2CH_2COOH$$

Linoleic Acid

$$CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_2CH{=}CHCH_2-CH_2CH_2CH_2CH_2CH_2CH_2COOH$$

Linolenic Acid

$$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2-CH_2CH_2CH_2CH_2CH_2CH_2COOH$$

The variation in chemical unsaturation is accompanied, by necessity, with changes in the content of various structural groups. It is obvious, for example, that as the number of double bonds in the foregoing $C_{18}$-fatty acid structures increases, the number of —CH=, —$CH_2$C= and =$CCH_2$C= groups increases as well, while the number of —$CH_2$— groups decreases. The number of $CH_3$— and —$CH_2$COO groups remains unchanged. Table I shows the composition of various fatty acids which are of interest in the alkyd chemistry.

For oils (Table II), the content of the structural groups is determined by the type and content of fatty acids in the oil. Since data on the composition of oils may vary according to the source of oil as well as the source of information, the data that have been used in our calculations are shown in Table VII in the Appendix, together with the calculation outlines.

As illustrated in Table II, the ratio of —$CH_2$— groups to =$CCH_2$C= groups varies substantially for different oils. Consequently, any technique which is capable of determining the content of —$CH_2$— groups relatively to the content of =$CCH_2$C= groups is suitable for the oil identification. NMR spectroscopy[9] is in principle the best technique for this purpose.

When a chemical is studied by NMR spectroscopy, the hydrogen atoms in the chemical give rise to NMR spectral peaks whose positions are determined by the structural environment of the hydrogens, and the relative peak areas are determined by relative numbers of the hydrogen atoms. Table III explains the NMR spectra of oils and alkyds. The peak positions indicated in the table may change in different solvents, but the order of the peaks and their mutual distances should

* For the sake of brevity, the following simplifications have been made in printing structural formulas throughout the following text: (1) Nonrelevant hydrogen atoms are omitted. (2) Hydrocarbon groups that are attached to a structural group of concern and contain no double bond are not shown but their presence is indicated by a bond(s). For instance, —$CH_2$C= refers to the underlined hydrogens in the structural group . . . $CH_2$—$CH_2$CH=CH. . . .

Table I
Composition of Fatty Acids by Structural Groups

| Group | No. of groups in acid | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Caprylic | Capric | Lauric | Myristic | Palmitic | Palmitoleic | Margaric | Stearic | Oleic | Linoleic | Linolenic | Eleostearic | Arachidic | Behenic | Lignoceric |
| $CH_3$— | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| —$CH_2$— | 5 | 7 | 9 | 11 | 13 | 9 | 14 | 15 | 11 | 8 | 5 | 7 | 17 | 19 | 21 |
| —$CH_2C$= | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 2 | 2 | 2 | 2 | 0 | 0 | 0 |
| —$CH_2COO$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| =$CCH_2C$= | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 2 | 0 | 0 | 0 | 0 |
| —CH= | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 2 | 4 | 6 | 2 | 0 | 0 | 0 |
| —CH= (conj.) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 0 | 0 |

TABLE II
Composition of Oils by Structural Groups[a]

| Group | No. of groups in oil | | | | |
|---|---|---|---|---|---|
| | Linseed | Soybean | TOFA | Tung | Coconut |
| $CH_3$— | 3 | 3 | 3 | 3 | 3 |
| —$CH_2$— | 23 | 28 | 29 | 23 | 30 |
| —$CH_2C$= | 5.4 | 5.1 | 5.4 | 5.7 | 0.5 |
| —$CH_2COO$— | 3 | 3 | 3 | 3 | 3 |
| =$CCH_2C$= | 3.6 | 2.1 | 1.4 | 0.3 | 0.06 |
| —CH= | 13 | 9 | 8 | 6.3 | 0.7 |
| —CH=(conj.) | 0 | 0 | 0 | 9.6 | 0 |
| $\frac{(-CH_2-)}{(=C\ CH_2C=)}$ | 6.4 | 13.3 | 21 | 77 | 500 |

[a] Composition of oils by fatty acids on which this table is based is given in Table VII.

TABLE III
Interpretation of NMR Spectra of Oils and Alkyds[a]

| Group | $\partial$, ppm[b] | Note | Origin |
|---|---|---|---|
| | | Oils | |
| $CH_3$— | 0.5 | | fatty acids |
| —$CH_2$— | 0.9 | largest peak | fatty acids |
| —$CH_2C$= | 1.6 | | fatty acids |
| —$CH_2COO$— | 1.9 | doublet | fatty acids |
| =$CCH_2C$= | 2.4 | | fatty acids |
| —$CH_2OCO$— | 3.5–4.5 | may contain OH peak | glycerol, pentaerythritol, glycols |
| >CHOCO— | 4.9 | | glycerol |
| —CH= | 4.9 | | fatty acids |
| —CH= (conj.) | 5.3–6.0 | | fatty acids |
| | | Additional Peaks in Alkyds | |
| Ar-H | 7.2 | | *o*-phthalic |
| Ar-H | 7.2–8.5 | three peaks | isophthalic |

[a] 60 MHz; deuterated acetone.

[b] The $\partial$ values may vary according to the solvent(s) used; the order of peaks and their mutual distances, however, should remain unchanged.

remain unchanged. For the identification of oil, the —$CH_2$— and =$CCH_2C$= peaks are easily recognized and evaluated. The —$CH_2$— peak is used also for the quantitative determination of oil. In some cases, the evaluation of other peaks may be helpful or necessary. Thus the Ar-H peak(s) is used for the identification and quantitative determination of the phthalic component. The —$CH_2OCO$— peak may be used for the quantitative determination of polyols when their identity is known. The —$CH_2C$= peak distinguishes between coconut oil and tallow. Probably other examples could be found in practice.

## NMR SPECTRA OF OILS AND ALKYDS

Figures 1, 2, and 3 show NMR spectra of TOFA, soybean, and linseed oils, respectively. The peak at 0.8–0.9 ppm corresponds to the terminal methyl groups in fatty acids. The huge peak at 1.2–1.4 ppm originates from the methylene groups surrounded by single-bonded carbon atoms, —$CH_2$—. These groups usually form the bulk of the fatty acid chain. The methylene groups

attached to a double-bonded carbon atom, $—CH_2C=$, give rise to the peak at 1.9–2.1 ppm. The absence of this peak would indicate that the analyzed sample contains only saturated fatty acids, e.g., such as coconut oil fatty acids. Figure 4 shows an NMR spectrum of coconut oil for illustration. The doublet at 2.1–2.3 ppm is brought about by the methylene groups next to the carboxyl groups, $—CH_2COO—$. The peak at 2.6–2.8 ppm corresponds to the methylene groups surrounded by two double-bonded carbon atoms, $=CCH_2C=$. Saturated fatty acids and acids with one double bond do not give rise to this peak. It is therefore absent in the spectra of coconut oil (Fig. 4) and tallow (Fig. 5). The NMR peak around 4 ppm is made by the methylene groups attached to an oxygen atom which is immediately followed by the carbonyl group, $—CH_2OCO—$. Since this group arises from esterification, the 4 ppm peak is not present in fatty acids (Figs. 1 and 5). The peak just over 5 ppm is made by the hydrogens on double-bonded carbon atoms, $—CH=$, and by the hydrogen on the middle carbon atom in a glyceride, $>CHOCO—$. The conjugated double bonds in fatty acids give rise to a series of peaks in the range from 5.5 to 6.4 ppm. Figures 6 and 7 illustrate this in cases of tung oil and dehydrated castor oil, respectively.

NMR spectra of resins made of fatty acids or oils carry all the foregoing

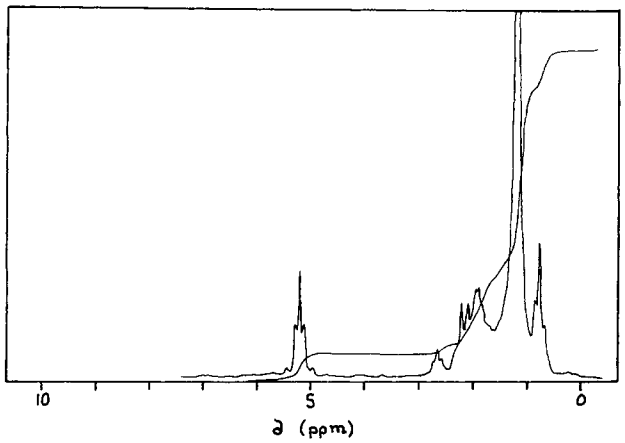


Fig. 1. NMR spectrum of TOFA (in deuterated chloroform).

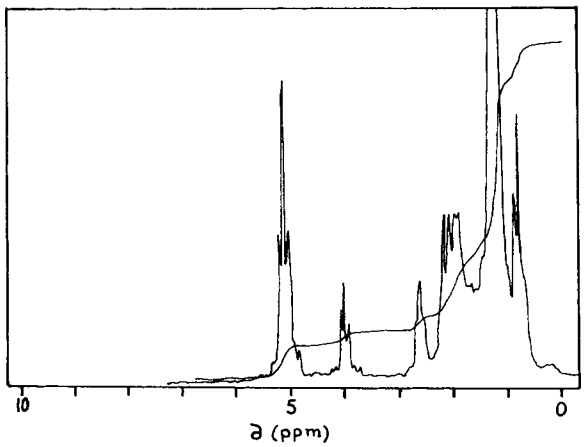


Fig. 2. NMR spectrum of soybean oil (in deuterated chloroform).

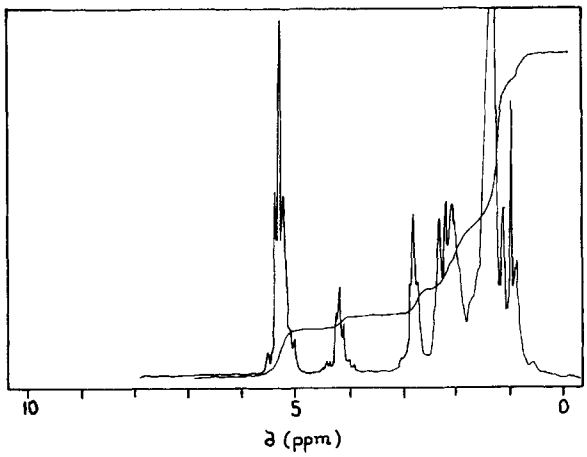


Fig. 3. NMR spectrum of linseed oil (in deuterated chloroform).

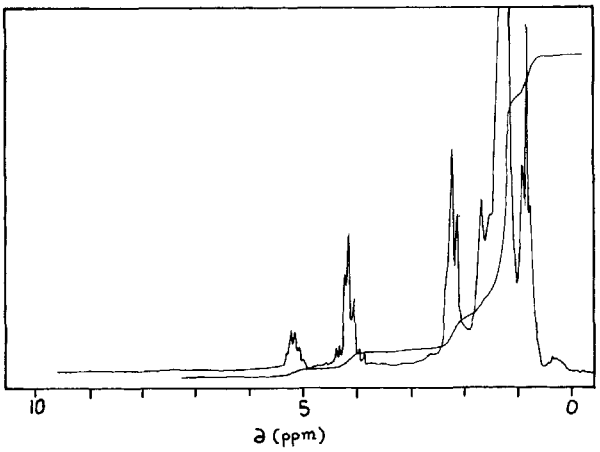


Fig. 4. NMR spectrum of coconut oil (in deuterated chloroform).

characteristics usually unchanged and unperturbed. The spectra in Figures 8 to 11 belong to an alkyd, diisocyanate-modified alkyd, alkyd modified with some glycols, and an oil-modified urethane, respectively. In all cases, the $—CH_2—$ and $=CCH_2C=$ peak areas can be easily evaluated.

As for the choice of solvent for a sample to be analyzed, it is advantageous to use deuterated chloroform rather than deuterated acetone, since traces of acetone which may be present in deuterated acetone appear on the NMR spectrum at the same position as the $—CH_2C=$ peak, making the evaluation of this peak impossible. Chloroform, on the other hand, appears as a peak of insignificant size at 7.1–7.4 ppm, causing no interference with the fatty acid spectrum and only negligible interference with the phthalic anhydride peak.

## ASSESSMENT OF THE TECHNIQUES

The NMR techniques for the identification of oils have been assessed by applying the techniques to samples of known identities. The samples employed were oils, oil fatty acids, alkyds, and a urethane. Numerical evaluation of the

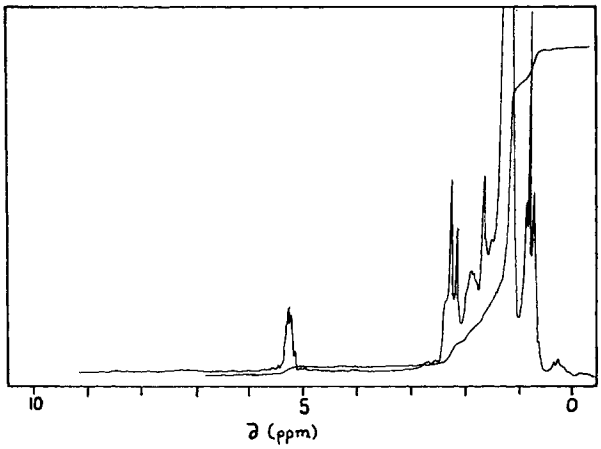


Fig. 5. NMR spectrum of tallow fatty acids (in deuterated chloroform).

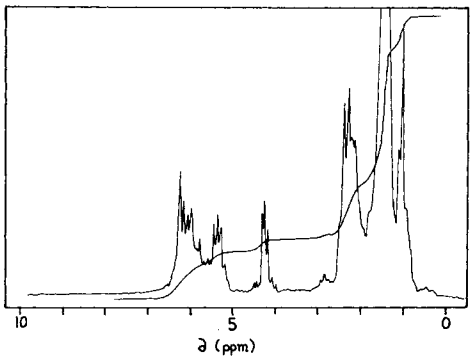


Fig. 6. NMR spectrum of tung oil (in deuterated chloroform).

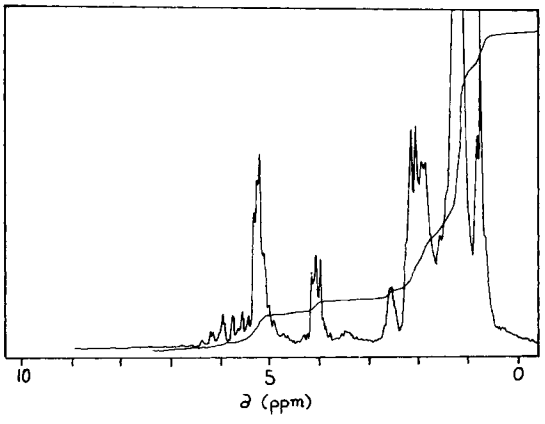


Fig. 7. NMR spectrum of dehydrated castor oil (in deuterated chloroform).

(—$CH_2$—)/(=$CCH_2C$=) peak area ratio and comparison of the experimental results with theoretical values are presented in Table IV.

Generally, the experimental results are in good agreement with the values predicted theoretically. The slight deviations, as observed, for example, with linseed-based substances, can be tolerated since the deviations are too small to

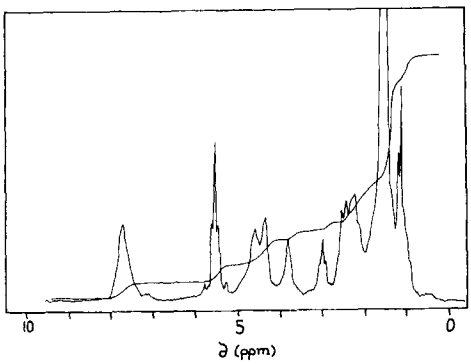


Fig. 8. NMR spectrum of alkyd (in deuterated chloroform).

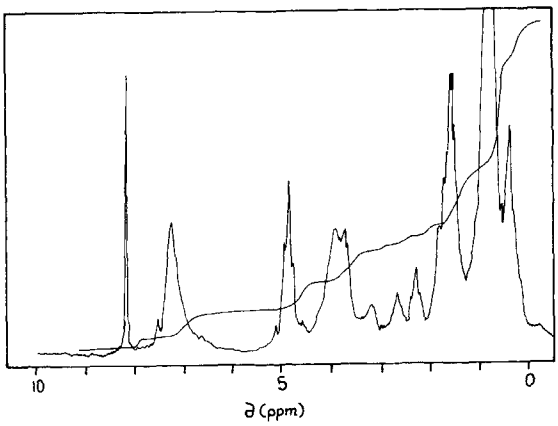


Fig. 9. NMR spectrum of isocyanate-modified alkyd (in deuterated acetone).

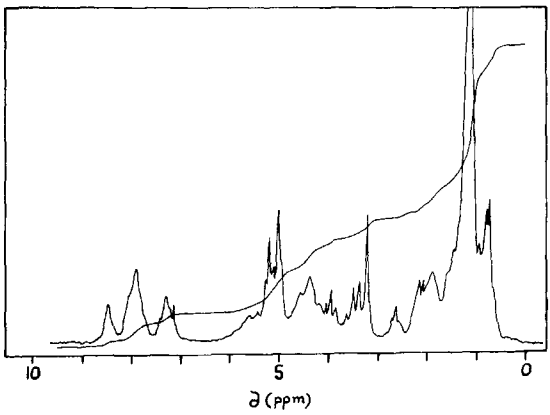


Fig. 10. NMR spectrum of glycol-modified alkyd (in deuterated chloroform).

cause ambiguity in distinguishing among soybean, linseed, and tall oil fatty acids, which are of main interest in the majority of alkyds.

Identification of oil by the NMR techniques will be made mostly from the peak area ratio $(—CH_2—)/(=CH_2C=)$. Values of the ratio for various oils are presented in Table V. In some cases, however, other peaks may be of interest. Thus, both coconut oil and tallow (Figs. 4 and 5, respectively) have virtually no

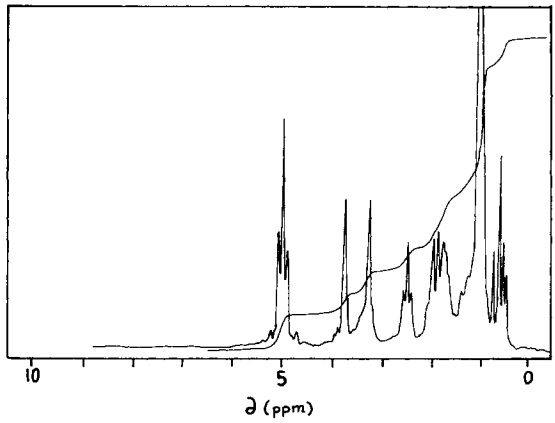


Fig. 11. NMR spectrum of oil-modified urethane (in deuterated acetone).

TABLE IV
Assessment of the NMR Techniques of Oil Identification

| Compound | (—$CH_2$—)/(=$CCH_2C$=) Ratio | |
|---|---|---|
| | Calculated | Found |
| Linseed fatty acids | 6.4 | 6.8 |
| Linseed oil | 6.4 | 6.0 |
| Linseed oil urethane | 6.4 | 5.8 |
| Soybean fatty acids | 13.3 | 14 |
| Soybean oil | 13.3 | 12 |
| Soybean oil alkyds (different samples) | 13.3 | 12, 13, 14, 14 |
| TOFA | 21 | 21 |
| TOFA alkyd | 21 | 21 |
| Soybean + linseed oil (1:1) alkyd | 9.8 | 9.6 |

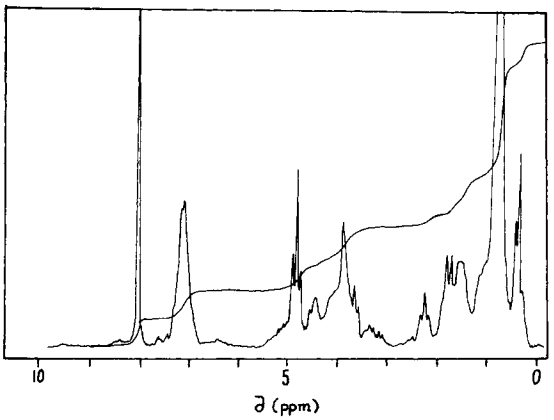


Fig. 12. NMR spectrum of alkyd with pyrazine (in deuterated acetone).

=$CCH_2C$= peak because of the very low content of linoleic and linolenic acids in their compositions. Tallow, however, has a high content of oleic acid in contrast to coconut oil, and, as a result, the NMR spectrum of tallow contains the —$CH_2C$= peak while this peak is virtually missing in the NMR spectrum of coconut oil. Another helpful NMR absorption can be that arising from the conjugated double bonds which would indicate tung oil and/or dehydrated castor oil (Figs. 6 and 7, respectively).

## COMPLETE ANALYSIS OF ALKYD

Figure 12 illustrates an NMR spectrum of alkyd resin based upon soybean oil, glycerol, and phthalic anhydride. The significance of the spectral peaks has been explained in Table III. Additionally, the peak at 8 ppm corresponds to the hydrogens in pyrazine; a known amount of pyrazine was added to the alkyd solids before analysis in order for one to be able to perform the quantitative evaluation of the spectrum.

Generally, the content of component C in a resin can be calculated from an NMR spectrum according to the following formula:

$$\% \text{ C} = \frac{W_{\text{pyr}}}{W_{\text{resin}}} \frac{(\text{MW})_{\text{C}}}{80} \frac{A_{\text{H}}/N_{\text{H}}}{A_{\text{pyr}}/4} \times 100$$

where $W_{\text{pyr}}$ and $W_{\text{resin}}$ are weights of pyrazine and resin, respectively, expressed in the same units; $(\text{MW})_{\text{C}}$ is molecular weight of component C; $A_{\text{H}}$ is the peak area for hydrogens of a particular identity in component C (e.g., $-CH_2-$ in fatty acids); $N_{\text{H}}$ is the number of hydrogens of that particular identity in one molecule of component C; and $A_{\text{pyr}}$ is the peak area for pyrazine.

Experimental arrangement for the case demonstrated was as follows. Solids of the alkyd were isolated by drying. A sample for the NMR analysis was prepared by mixing 215.6 mg solids with 35.6 mg pyrazine, and by dissolving the mixture in deuterated acetone.

The spectrum provided the results shown in Table VI. The peak area for $-CH_2-$ when divided by the peak area for $=CCH_2C=$ yielded a value 14.4, indicating the presence of soybean fatty acids. Knowing the identity of fatty acids, the oil content was evaluated according to the foregoing equation for % C:

$$\% \text{ soybean oil} = \frac{35.6}{215.6} \frac{878}{80} \frac{72/56}{16.6/4} \times 100 = 56.1$$

The content of glycerin was evaluated from the peak area ranging from 3.5 to

TABLE V
$(-CH_2-)/(=CCH_2C=)$ Ratio for Various Oils[a]

| Oil | $(-CH_2-)/(=CCH_2C=)$ ratio |
|---|---|
| Perilla | 4.9 |
| Linseed | 6.4 |
| Hempseed | 7.7 |
| Safflower | 11.7 |
| Soybean | 13.3 |
| Grapeseed | 13.9 |
| Sunflower | 17.4 |
| Corn | 18.1 |
| TOFA | 21–23 |
| Cottonseed | 26 |
| Peanut | 51 |
| Olive | 54 |
| Tung | 77 |
| Coconut | 500 |
| Tallow | Extremely high |

[a] The composition of oils on which this table is based is given in Table VII.

TABLE VI

| Peak, ppm | Identity | Peak area, arbitrary units |
|---|---|---|
| 0.75 | $-CH_2-$ | 72 |
| 2.25 | $=CCH_2C=$ | 5.0 |
| 3.5–4.6 | $-CH_2OCO-$ | 24.0 |
| 7.2 | $A_r-H$ | 17.5 |
| 8.0 | pyrazine | 16.6 |

4.6 ppm (the identity of polyol has to be known in advance since the NMR techniques do not distinguish reliably glycerin from pentaerythritol):

$$\% \text{ glycerin} = \frac{35.6}{215.6}\frac{92}{80}\frac{24.0/4}{16.6/4} \times 100 = 27.5$$

Of this amount, 5.9% was accounted for as coming from soybean oil:

$$\% \text{ glycerin from oil} = \% \text{ oil} \frac{\text{mol. weight of glycerin}}{\text{mol. weight of oil}} = 56.1 \frac{92}{878} = 5.9$$

The remaining 21.6% was considered as free glycerin in the original formulation.

The phthalic anhydride content was evaluated from the peak area at 7.2 ppm:

$$\% \text{ PA} = \frac{35.6}{215.6}\frac{148}{80}\frac{17.5/4}{16.6/4} \times 100 = 32.2$$

$$\text{total } \% = 56.1 + 21.6 + 32.2 = 109.9$$

At least two factors account for the total being more than 100%. Firstly, the calculations use molecular weights of acids and alcohols while the esters are lighter by the water of condensation. This causes the results to be higher. Secondly, an error in weighing is reflected in the final results by the same relative values, i.e., all the results are either higher or lower, but not random. In the final step, therefore, the following procedure can be used to correct the total to 100%:

$$\% \text{ soybean oil} = 56.1 \frac{100}{109.9} = 51.0$$

$$\% \text{ glycerin} = 21.6 \frac{100}{109.9} = 19.6$$

$$\% \text{ PA} = 32.2 \frac{100}{109.9} = 29.3$$

These figures compare well with the actual formulation data: 50% soybean oil, 20% glycerin, and 30% phthalic anhydride. Three different batches of the same formulation were cooked in our laboratory, and each of the resins was analyzed in the same way. The calculated contents of the components were always within a 1% deviation (absclute) from the actual formulation.

TABLE VII
Composition of Oils

| Acid | No. of acid groups in oil | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Coconut | Corn | Cottonseed | Grapeseed | Hempseed | Linseed | Olive | Peanut | Perilla | Safflower | Soybean | Sunflower | Tallow | TOFA | Tung |
| Caprylic | 6 | | | | | | | | | | | | | | |
| Capric | 6 | | | | | | | | | | | | | | |
| Lauric | 44 | | | | | | | | | | | | | | |
| Myristic | 18 | | 1 | | | | | | | | | | 3 | | |
| Palmitic | 11 | 13 | 29 | 9 | 6 | 6 | 14 | 6 | 7 | 8 | 11 | 11 | 27 | 5 | 4 |
| Palmitoleic | | | 2 | | | | 2 | | | | | | 3 | | |
| Margaric | | | | | | | | | | | | | 2 | | |
| Stearic | 6 | 4 | 4 | 4 | 2 | 4 | 2 | 5 | 2 | 3 | 4 | 6 | 27 | 3 | 1 |
| Oleic | 7 | 29 | 24 | 20 | 12 | 22 | 64 | 61 | 13 | 13 | 25 | 29 | 38 | 46 | 8 |
| Linoleic | 2 | 54 | 40 | 67 | 55 | 16 | 16 | 22 | 14 | 75 | 51 | 52 | | 41 | 4 |
| Linolenic | | | | | 25 | 52 | 2 | | 64 | 1 | 9 | 2 | | 3 | 3 |
| Eleostearic | | | | | | | | | | | | | | | 80 |
| Arachidic | | | | | | | | 2 | | | | | | 2 | |
| Behenic | | | | | | | | 3 | | | | | | | |
| Lignoceric | | | | | | | | 1 | | | | | | | |

## CONCLUSIONS

The NMR techniques can reliably discriminate among the oils most typically used in the production of alkyds, such as soybean and linseed oils and tall oil fatty acids, on the basis of the $(—CH_2—)/(=CCH_2C=)$ ratio. The techniques have sound accuracy and reproducibility. In comparison with the widely used gas chromatography techniques for the identification of oil, the NMR analysis is much faster (typically less than 1 hr) since it does not require that the sample be broken into its single alcohol and acid components. Resins are analyzed in the reacted state.

In some cases the NMR techniques could prove to be more sensitive than gas chromatography. For example, soybean oil can be reliably distinguished from sunflower oil on the basis of $(—CH_2—)/(=CCH_2C=)$ ratios, which are 13.3 and 17.4, respectively. A gas chromatogram, on the other hand, would provide a poor distinction between the two oils.

Table V lists $(—CH_2—)/(=CCH_2C=)$ ratios for various oils. Although the ratios are rather similar for some oils and the distinction between two neighbors in the table may be difficult, the typical alkyd-utilized oils such as linseed, soybean, and tung oils and tall oil fatty acids can be distinguished very reliably.

It may be useful to point out that some oils can be identified by NMR spectroscopy according to other spectral characteristics than the $(—CH_2—)/(=CCH_2C=)$ ratio. Tung oil, for example, is typical by its conjugated double bonds which give rise to NMR peaks between 5.3 and 5.8 ppm (relative to the values in Table III). Similar but less pronounced characteristics apply to dehydrated castor oil. Another example is the discrimination between coconut oil and tallow. Both substances have an extremely low content of $=CCH_2C=$ groups, and the distinction on the basis of the $(—CH_2—)/(=CCH_2C=)$ ratio is impossible. The content of $—CH_2C=$ groups, however, is soundly different in these two materials, which provides a reliable means of discrimination between coconut oil and tallow.

It may also be useful for the reader to consult the publication by Yeagle on NMR analysis of polyesters,[10] which assigns NMR peaks to various glycols that may be occasionally used in alkyds.

## Appendix

### Calculation of the Composition of Oils by Structural Groups

$$\text{No. of groups} = \frac{3}{100} \sum_{\text{all acids}} (\text{no. of groups in acid}) \times (\% \text{ acid in oil})$$

Example: Soybean oil of the composition given in Table VII:

$$(—CH_3)= \frac{3}{100}[(1 \times 11) + (1 \times 4) + (1 \times 25) + (1 \times 51) + (1 \times 9)] = 3$$

$$(—CH_2—) = \frac{3}{100}[(13 \times 11) + (15 \times 4) + (11 \times 25) + (8 \times 51) + (5 \times 9)] = 27.9 \approx 28$$

etc.

## References

1. *High Polymers,* Vol. XII, Analytical Chemistry of Polymers, Part I, G. M. Kline, Ed., Interscience, New York, 1966, Chap. II.
2. G. G. Esposito and M. H. Swann, *Anal. Chem.,* **32**(1), 49 (1960).
3. W. L. Zielinski, W. V. Moseley, and R. C. Bricker, *Official Digest,* 622 (May 1961).
4. G. G. Esposito and M. H. Swann, *Anal. Chem.,* **34**(9), 1048 (1962).
5. J. C. West, *Anal. Chem.,* **47**(9), 1708 (1975).
6. American Society for Testing and Materials, Baltimore, Md., ASTM D2455-69.
7. American Society for Testing and Materials, Baltimore, Md., ASTM D2245-72.
8. C. J. Opp, *Official Digest,* 42 (January 1964).
9. D. W. Matheson, Ed., *Nuclear Magnetic Resonance for Organic Chemists,* Academic Press, New York, 1967.
10. M. L. Yeagle, *J. Paint Technol.,* **42,** 472 (1970).

Received August 10, 1977
Revised September 20, 1977