absorption maximum of the TBA-malonaldehyde complex. Paper chromatography has shown that both compounds give identical spots. Until this compound derived from degradation of TBA is identified, it cannot be said with certainty whether it is malonaldehyde or other 3-carbon fragment or decomposition products of either thiourea or malonic acid interacting with TBA to give a compound similar to the TBA-malonaldehyde complex and absorbing at the same wavelength. It should be remembered that even traces of a compound with a highly chromophoric group can give a color with a distinct visible spectrum, which may not be detected by infrared if it is present in concentration less than 5% of the mixture.

It has been reported in the literature that many compounds react with TBA to give complexes absorbing at 450 and 490 mμ (2,3,4–13,16–19,23–25,28,29). In view of the fact that pure TBA heated with acids and even twice recrystallized TBA absorbs at the same wavelength, it has to be determined whether the reported compounds really react with TBA or whether changes in the structure of TBA have been assumed to be other compounds, especially when the blanks were treated differently from the samples.

In view of the fact that highly significant correlations have been obtained between TBA numbers and taste-panel results on various oxidized foods, the results of this work should not be construed as a suggestion to discard the TBA test for determination of rancidity in oxidized foods. They merely point out that more care should be taken in the conditions of the test and in the treatment of the blank so that the results obtained are really quantitative.

Work is under way in this laboratory for the development of a TBA test without the need of acid-heat treatment for the determination of malonaldehyde in rancid foods.

Acknowledgments

The authors wish to express their gratitude to J. R. Brunner and P. A. Markakis of the Food Science Department for the use of various instruments. The help of G. J. Karabatsos of the Chemistry Department for the interpretation of the IR spectra is gratefully acknowledged.

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Application of Infrared Spectroscopy to the Analysis of Primary Fatty Amide Mixtures

W. E. LINK and K. M. BUSWELL, Archer-Daniels-Midland Company, Minneapolis, Minnesota

The composition of fatty amide mixtures, containing mostly simple primary amides, has been studied by means of an infrared method utilizing the Amide I carbonyl absorption band. In dilute chloroform solution the amides, $CH_3(CH_2)nCONH_2$, absorb consistently at about 5.95 μ and do not display apparent association or enolization. The concentration of unsubstituted amides has been quantitatively related to the intensity of the Amide I band throughout the range from 1 to 100%. With the scale expansion the sensitivity of the method may be extended to 0.03% without difficulty.

The influence of certain impurities on the intensity of the Amide I band is discussed. Carbonyl absorption from fatty acids, ketones, and esters constitutes an interference. *N*-monosubstituted amides also contribute to the absorption observed at 5.95 μ, but their presence is indicated by additional absorption at about 6.60 μ.

The determination of small amounts of amides in amines may be accomplished by measuring the total Amide I absorption of a sample dissolved in tetrachloroethylene and relating this absorption to that of known mixtures run under identical conditions.

CHEMICAL METHODS, which provide dependable and precise analyses with fatty amines, are less successful with fatty amides, for the usual basicity of the nitrogen, upon which many functional analyses are based, is neutralized by the presence of the acyl group. A variety of methods are available, nevertheless, for the study of primary amide mixtures.

Vigorous treatment with acid (8) or alkali (17) will hydrolyze amides so that the resulting amine or ammonia may be liberated, distilled, and finally titrated as in a Kjeldahl determination. Olsen (13) has presented a saponification value procedure which eliminates the interference of esters. The reduction of amides to amines with lithium aluminum hydride is feasible. In this procedure, by Siggia (18), the amine is steam distilled and titrated with standard acid. Nitriles are a serious interference. A number of investigators (2,14,19,21) have studied the reaction of hydroxylamine with amides to form hydroxamic acids which can be estimated by color reaction

with ferric ion. The interferences with this procedure include esters, carboxylic acids, acid chlorides, imides, and nitriles. Mercury compounds (17) of the fatty acid amides have been used to characterize and to determine amides, but the method is not attractive for routine application. By means of a modified glass-calomel electrode couple, amides may be titrated potentiometrically (22) in a medium of acetic anhydride with perchloric acid in dioxane as the titrant.

Analysis of primary amides of mono- and dibasic aliphatic acids may be accomplished by reaction with 3,5-dinitrobenzoyl chloride (12). The amount of amide may be calculated from a titration of the liberated hydrochloric acid. Acids and water interfere.

Preliminary work in our laboratory suggested the feasibility of an infrared method based on the CO absorption for the analysis of simple primary fatty amide mixtures. The results of a study of such a method are presented in the hope that they will provide the basis for an acceptable procedure and incentive for further study.

Simple primary amides examined in the solid state (Fig. 1) show a strong absorption band in the infrared region near 6.06 μ (1). In dilute solution in dioxane or chloroform the amides appear to be monomeric and absorb in the region from 5.92 to 5.95 μ (16). This Amide I band, commonly assigned to carbonyl absorption, is also exhibited by simple N-mono-substituted amides at about 5.95 μ. In addition to the CO absorption, unsubstituted amides exhibit in dilute chloroform solution a band at about 6.20 μ, attributed to a combination of OCN and NH vibrations (5,6). In *N*-monosubstituted amides this Amide II band shifts to about 6.60 μ (16). In *N,N*-disubstituted amides the Amide I band falls in the range of 6.00 to 6.07 μ in nonpolar solvents and shows no Amide II band (16). In Fig. 2 are shown the pertinent portions of spectra of a typical unsubstituted amide, lauramide, in dilute chloroform and those of *N*-lauryllauramide in dilute tetrachloroethylene solution.

Not much is known about factors which influence the intensity of the carbonyl absorption. Some consistency was found for the extinction coefficients of simple amide CO absorptions by Richards and Burton (15). Lenormant (3,4) states that the intensity of the CO band is subject to variation and can be changed by the alkalinity of the solution. Recently Spell and Eddy (20) have determined oleyl amide in extracts from polyethylene and have reported the molar absorptivity of the 5.9 μ band to be 346 l. per mole-cm. Miller reported a value of 444 for lauramide (11). Further information regarding extinction coefficients of the Amide I band in fatty amides is lacking, but work in this field is clearly desirable.

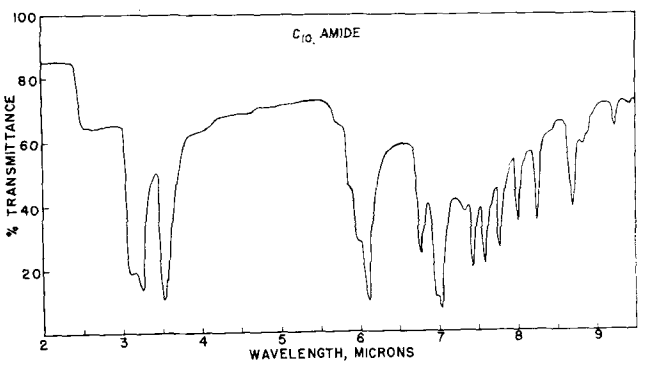

FIG. 1. Infrared spectra of capramide from 2 to 10 microns, solid film.

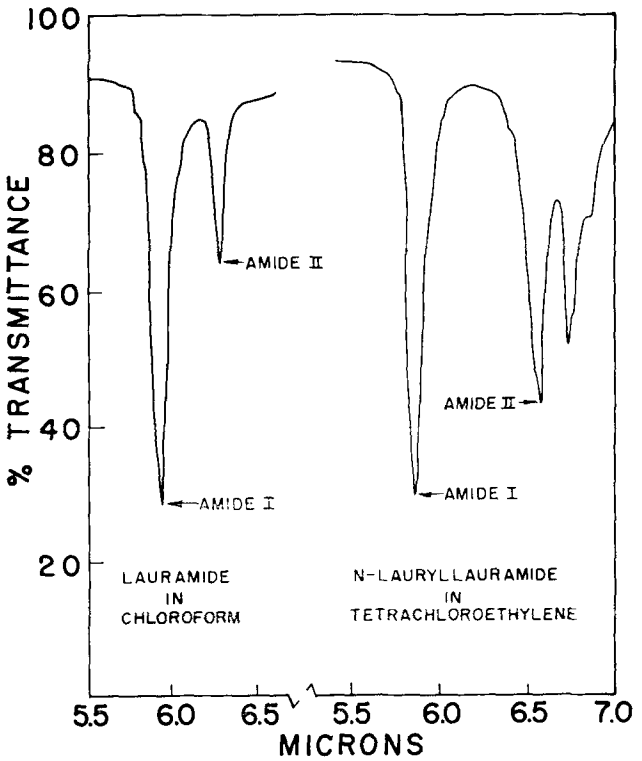

FIG. 2. Infrared spectra of lauramide, 2.00 g./l. in chloroform *vs.* chloroform; *N*-lauryllauramide, 4.20 g./l. in tetrachloroethylene *vs.* tetrachloroethylene, 1.0 mm. cell.

Experimental

Preparation of Standards. The standard amides used in this study, with chain lengths of 10, 12, 14, 16, and 18, were prepared from commercially available products (Adogens, A-D-M Co.) by fractional crystallization from carbon tetrachloride, followed by a final crystallization from ethanol. The purity of each specimen was checked by thin layer chromatography on silicic acid plates according to the method of Malins and Mangold (10). Amides in amounts between 5 and 5,000 γ were used with a solvent mixture of 97 parts chloroform, 3 parts methanol, and 0.25 part 17 *N* ammonium hydroxide. The C_{10}, C_{12}, C_{14}, and C_{18} amides were found to contain small amounts of nitriles, less than 1%. This amount was substantiated by infrared spectra, using the band at 4.42 μ. The C_{16} and C_{18} amides also contained traces of fatty acids. All of the amides were at least 99% pure.

The chain length distributions of the amide standards were determined by gas-liquid chromatography. The amides were hydrolyzed with 7 *N* HCl to the corresponding fatty acids which were converted to methyl esters and analyzed. Essentially identical distributions were obtained through reduction of the amides with lithium aluminum hydride to amines and analysis of the amines by gas chromatographic procedures previously described (9). The compositions of the reference amides used to establish Beer-Lambert relationships are shown in Table I.

Instrument. A Perkin-Elmer 221 double beam spectrophotometer equipped with scale expansion and sodium chloride optics was used. Measurements were made in sodium chloride liquid absorption cells with a path of 1 mm., using analytical reagent grade tetrachloroethylene or chloroform as the solvent. These solvents were further purified by chromatography through silica gel.

TABLE I
Fatty Amide Standards

Homologue	GLC analysis	Mol. wt.	Molar extinction coefficient, K^a
Capramide	99%	171	497
Lauramide	98% C_{12}, 2% C_{14}	200	498
Myristamide	97.1% C_{14}, 1.9% C_{16}, 1.0% C_{12}	227	505
Palmitamide	91.4% C_{16}, 4.5% C_{18}, 1.5% C_{17}, 0.6% C_{15}, 2.0% C_{14}	256	509
Stearamide	91.3% C_{18}, 2.4% C_{20}, 0.6% C_{19}, 1.0% C_{17}, 4.7% C_{16}	282	500
			Av. 502

$$K^a = \frac{\text{optical density}}{(\text{con. in moles/l.})\,(\text{cell thickness in cm.})}$$

The infrared program used for high percentage amides consisted of scale 1X, a manual slit width of 52 μ, attenuator speed 11, gain 4.5, and suppression 10. For samples containing less than 1% amide, a scale expansion of 5X was used, with the automatic slit program of 980, attenuator 6, and suppression 10. The scanning speed was 2 min. per micron.

Procedure for High Percentage Amides. Samples (0.100 g.) of each of the standard amides were weighed into 50-ml. volumetric flasks and diluted to volume with chloroform. A 1.0 mm. cell was used to record the spectrum from 5.4 to 6.5 μ, with a matched cell with pure solvent as the reference. On the spectrum, a line was drawn tangent to the curve at about 5.73 and 6.05 μ to obtain the corrected absorbance (A). The cell factor (F) was determined as follows:

$$\frac{\text{Sample wt. (g./l.)}}{\text{Mol. wt. of sample}} = \text{moles/l. of sample}$$

$$F = \frac{A}{\text{Moles l. of sample}}$$

The average factor for the cell in use was determined. Table I shows the average molar extinction coefficient for each of the standard amides.

The Beer-Lambert relationship was found to be valid for concentrations of amides over a wide range as shown in Fig. 3. For the C_{14} amide measured as described previously this corresponds to concentrations of amide from 1 to 100 mg. per 50 ml.

Unknown mixtures of amides were analyzed exactly as described above. If the cell used for standardization is also used for the unknown sample the calculation may be made as follows:

$$\text{Moles/kg. amide} = \frac{A \times 50}{F \times \text{sample wt. in 50 ml.}}$$

$$\%\ \text{Amide} = \frac{\text{Actual moles/kg.}}{\text{Theor. moles/kg.}} \times 100$$

$$\text{Theor. moles/kg.} = \frac{1000}{\text{Mol. wt.}}$$

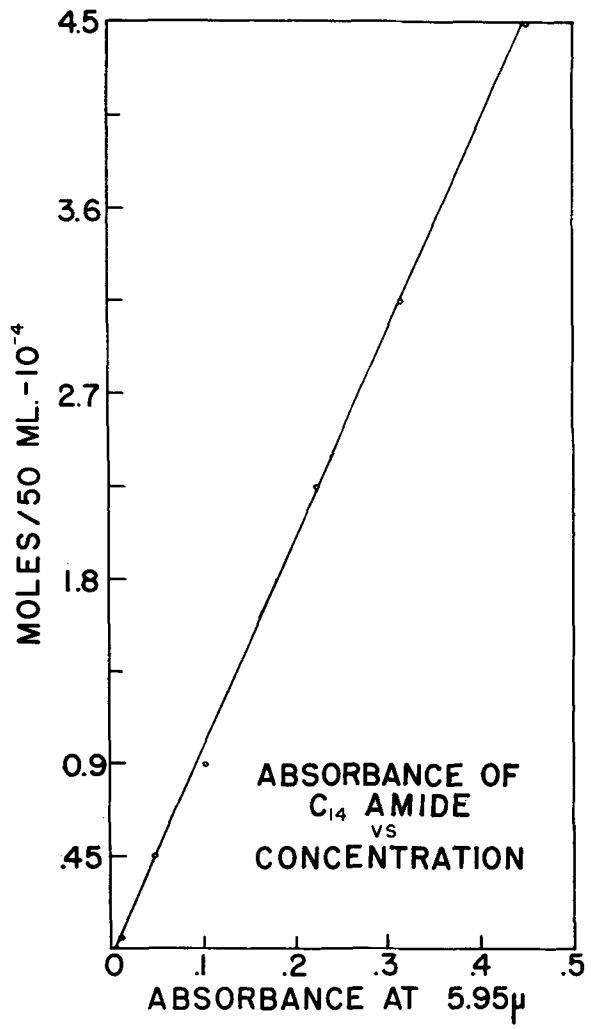

FIG. 3. Absorbance of myristamide at 5.95 microns as a function of concentration.

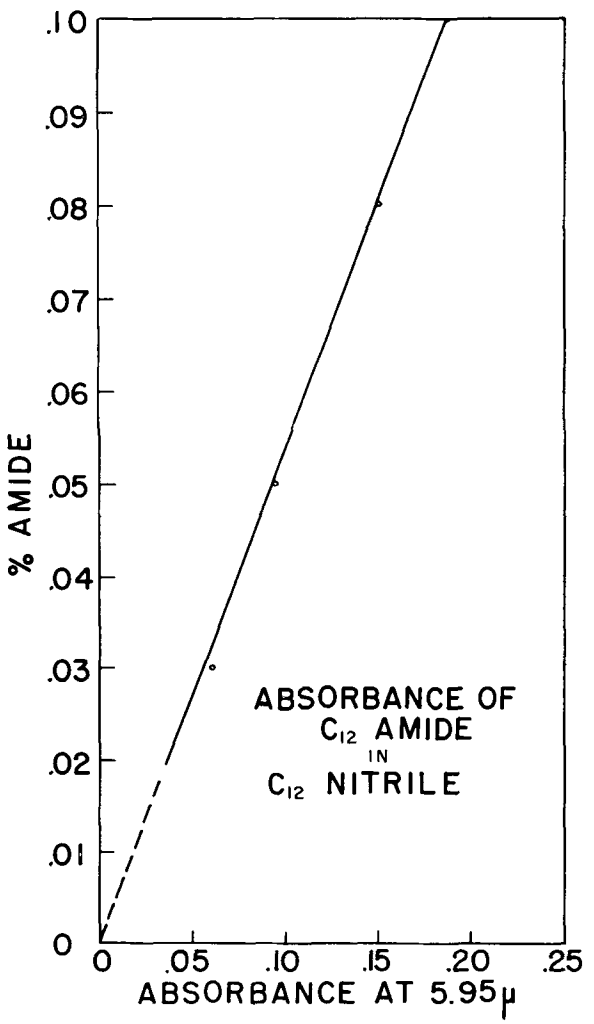

FIG. 4. Absorbance of lauramide at 5.95 microns as a function of concentration of amide in nitrile.

The molecular weight of the unknown may be determined from the percentage of nitrogen or by gas chromatography.

Procedure for Low Percentage Amides. With samples containing a low level of amide and a large amount of nitrile or other material which does not absorb in the region from 5.73 to 6.05 μ, scale expansion may be used to advantage. The calibration is carried out by the method described for high percentage amides except that the program of the instrument is changed to accommodate the 5X scale expansion. If the solubility of the sample permits, the amount of sample taken for analysis may be increased. With a 1-g. sample in 10 ml. of chlorform 5X expansion will easily permit the analysis of samples containing as little as 0.02% amide.

The sensitivity of the method is demonstrated in Fig. 4, which shows the relationship between the absorptivity at 5.95 μ and the amount of C_{12} amide in a C_{12} nitrile. Samples with an amide content of over 0.3% may be measured without the aid of scale expansion by adjusting the sample size. The amount of amide may be calculated in terms of a specific amide, as in Figure 3 or, as outlined in the procedure for high purity amides, in percentage of total amide if the molecular weight of the amide is known.

Results and Discussion

The Amide I peak is subject to a considerable shift in frequency when hydrogen bonding is broken. It is also liable to variations depending on the polarity of the solvent employed. The poor solubility of the fatty amides in most solvents does not offer the analyst much latitude. Both effects may be largely overcome through the use of extremely dilute solutions in chloroform and relatively large absorption cells. It is believed that there is no tendency of the ordinary amides to enolize under these conditions and that the amides are essentially monomeric. The absorbance at 5.95 μ was found however to decrease slightly with a rise in temperature of the absorption cell. This decrease with increasing temperature presumably indicates intramolecular bonding but could be a function of cell or solvent expansion. To minimize this effect, samples and cells were equilibrated at 25°C. for at least 15 min. and were run without delay after placement in the cell holder.

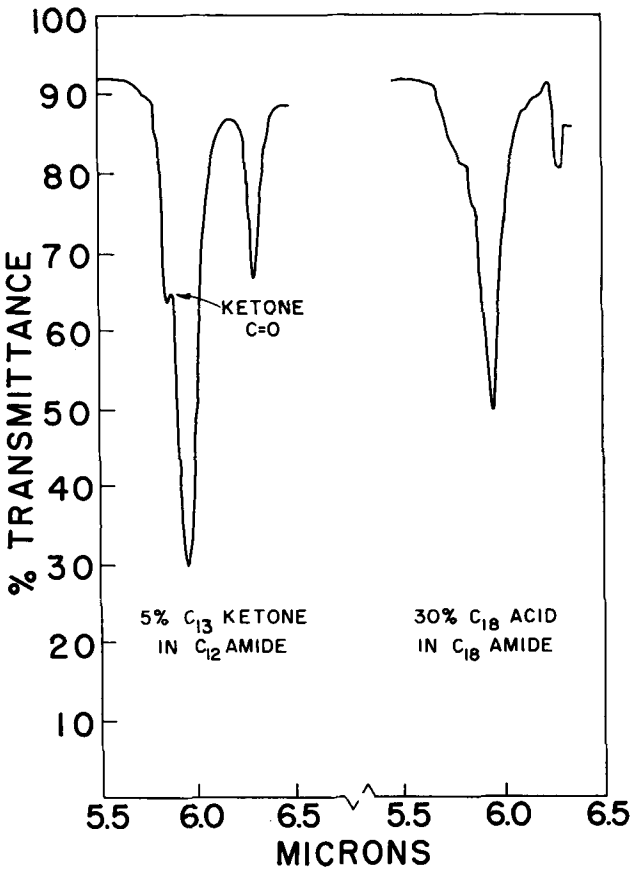

FIG. 5. Infrared spectra of a 5% w/w methyl undecyl ketone in lauramide, 2.00 g./l.; 30% w/w stearic acid in stearamide, 2.00 g./l.; in chloroform *vs.* chloroform, 1.0-mm. cell.

Carbonyl absorption from fatty ketones, acids, and esters contributes to the absorbance near 5.80 μ and may interfere with measurement of the Amide I band under certain conditions. Fatty ketones give rise to an absorption at about 5.83 μ which shows up as a shoulder on the Amide I band. Carbonyl absorption from fatty acids is evident as a broadening of the Amide I band when the level of acid is about 10% or more. Both of these effects are shown in Fig. 5. Known mixtures were analyzed for amide content to give the data in Tables II and III.

TABLE II
Effect of Ketone[a] in Amide Determination

% Amide		Error difference
Known	By analyses	
99	98.4	−0.6
95	95.0	0
80	82.0	+2.0
70	74.5	+4.5
50	53.7	+3.7
25	28.6	+3.6
10	13.8	+3.8

[a] Methyl undecyl ketone in lauramide.

TABLE III
Effect of Acid[a] in Amide Determination

% Amide		Error difference
Known	By analysis	
95	98.8	+ 3.8
90	93.2	+ 3.2
70	74.0	+ 4.0
50	54.5	+ 4.5
30	41.2	+11.2
10	20.1	+10.1

[a] Stearic acid in stearamide.

From these data, it may be concluded that up to 5% of ketone of similar chain length may be tolerated and further amounts give a fairly constant error, but increasing amounts of fatty acid give rise to a serious error. This may be partially overcome by a correction factor derived from data such as that presented above, or preferably the fatty acids may be removed through alkaline extraction of a chloroform solution of the amide.

Since esters are normally not found in fatty amides prepared from fatty acids, the interference of this type material has not been investigated. If glycerides are the starting materials, the influence of ester carbonyl absorption would have to be considered. It is not anticipated that esters would increase association of the amides in dilute solution.

N-monosubstituted amides also contribute to the absorption near 5.95 μ but the resulting band is readily resolved with sodium chloride optics and distinguished from the Amide II band of primary amides which falls at about 6.20 μ (see Fig. 2). A mixture of primary and secondary amides displays both bands,

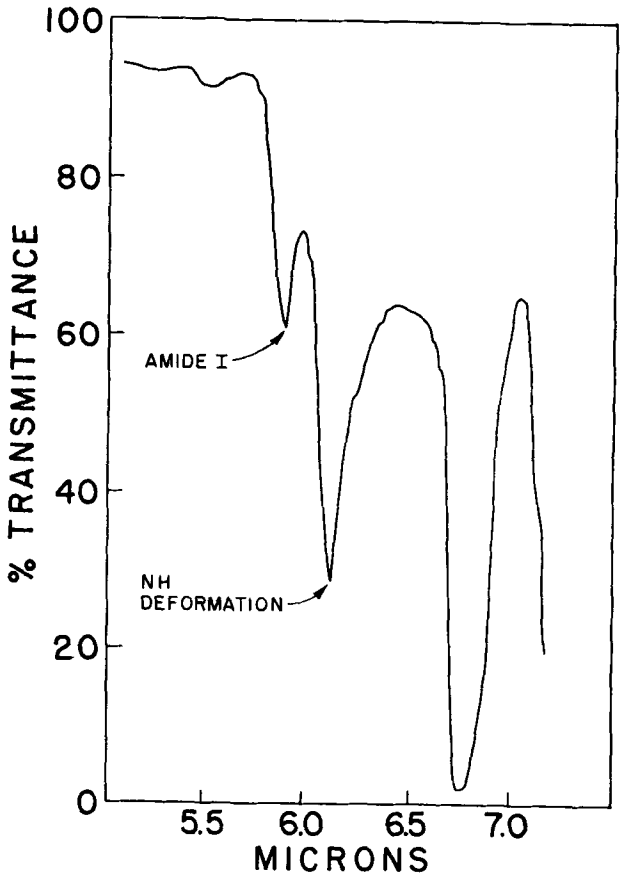

FIG. 6. Infrared spectra of 6.5 mg. lauramide and 500 mg. laurylamine in 10 ml. tetrachloroethylene *vs.* tetrachloroethylene, 1.0 mm. cell.

offering a method for quick qualitative identification. Chloroform is not a satisfactory solvent in this region, because of poor transmission.

Sufficient information is not yet available to permit the analysis of mixtures on this basis. Obviously, large amounts of secondary amides (or for that matter, tertiary) render the method for primary amides less useful.

In the determination of small amounts of amides in the presence of a large amount of primary amines an additional problem is encountered, although that associated with solubility is absent. A band is present in the simple amines near 6.06–6.29 μ (Fig. 6) that interferes with the measurement of the Amide I band by the baseline technique described earlier. A good correlation was found however between the amide content of an amine and the absorbance if the baseline were drawn from 5.65 to 6.55 μ. The absorbance of the Amide I band exhibited by small amounts of lauride, from 0.1% to 3.0%, in lauryl amine is shown in Fig. 7. These data were obtained with 0.50-g. samples in 10 ml. of solution, run in a 1.0-mm. cell, with tetrachloroethylene as the solvent. With suitable calibration, the technique may be extended to include other amides and mixtures of simple amides, but it must be emphasized that the known mixtures used for calibration must be similar in composition to the unknown material under analysis.

Conclusions

Although the method described is empirical, it is believed that it will provide useful quantitative data concerning amide mixtures. The method is rapid and reproducible, and one determination can easily be carried out in 30 min. In Table IV the results of replicate analyses of commercial samples are shown. An analysis of these and other data indicates that the standard deviation is 0.020, and that two single determinations performed in the same laboratory should not differ by more than .054 moles/kg. 95 times out of 100. The accuracy thus appears to be at least that of chemical methods.

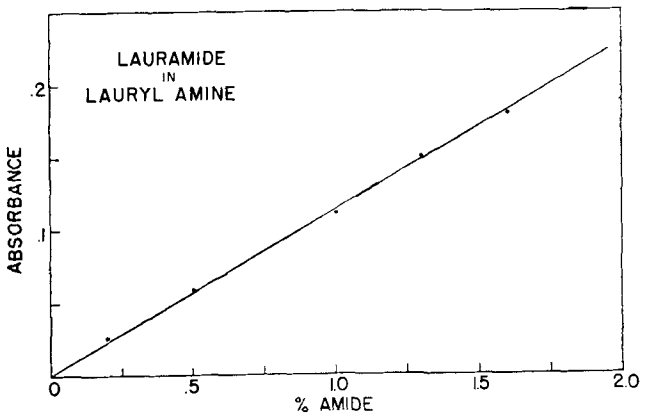

FIG. 7. Absorbance of lauramide at 5.95 μ as a function of concentration of lauramide in laurylamine.

Although useful for simple primary amide mixtures, the method should not be used indiscriminately, and the effect of interferences should be considered. Because of variations in instrument parameters which include slit programs, spectral purity and photometric response, it is not presently feasible to determine absolute absorbancies, and data obtained with one instrument may be translated to another only with difficulty. It is highly desirable therefore that calibration curves be established for each individual instrument.

TABLE IV
Analysis of Commercial Fatty Amides

Sample	Moles/kg. of amide	% Amide
Tallow amide	3.06	84.8
	3.06	84.8
	3.02	84.7
Fish amide	3.16	95.2
	3.18	95.8
	3.13	94.3
Oleyl amide	3.60	99.4
	3.61	99.7
Erucyl amide	3.05	99.5
	3.05	99.5

Acknowledgment

The authors are indebted to H. K. Mangold of the Hormel Institute, Austin, Minn., for the analysis of the amide standards by means of thin layer chromatography on silicic acid plates.

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Plant Scale Comparisons of Various Refining Methods for Cottonseed Oil

G. C. CAVANAGH, Research Department, Ranchers Cotton Oil, Fresno, California

Three different refining processes were commercially compared by processing 15,148 metric tons of cottonseed with free fatty acid content varying between 7.1% and 8.9%. All of the seed was prepressed and solvent extracted in the Sanbra plant at Bauru, Brazil. The Ranchers Miscella refining process operating on seed averaging 8.8% F.F.A. yielded more oil of lighter color per ton of seed processed than either of the other processes compared, even though the average F.F.A. of the seed processed during the Ranchers Miscella Refining test averaged 1.7% higher than the seed used in the Sanbra process and 1.1% higher than the average F.F.A. for the seed used in the Low Loss Refining test.

In another comparison, screw pressed oil, Modified Soda Ash refined was compared to Ranchers Miscella refining with seed containing about 0.5% F.F.A. The results showed 42% lower refining loss and a color of 3.5 Red Lovibond units less for Ranchers Miscella refined oil than for Modified Soda Ash refined oil.

The average cost of converting crude cottonseed oil to prime bleachable summer yellow oil by the miscella refining process described is 20.8¢ per hundred weight of oil (not including refining loss). These costs include the prorated cost of control laboratory, plant labor and supervision, fuel, power, chemicals, depreciation, taxes and insurance.

OF THE commercially significant edible vegetable oils processed, one of the most difficult to refine with respect to color removal is cottonseed oil (12). Vegetable oil refiners, processing cottonseed oil or similar highly pigmented oils by conventional methods, continuously compromise between high refining loss resulting from the use of strong caustic on the one hand and highly colored oils which meet with consumer resistance on the other. Re-refining and bleaching may improve the color of the product but these processes add to the production cost, decrease the yield of finished product and contribute to the instability of the finished product (1,8).

In April 1956 a paper was presented before the A.O.C.S. describing a new integrated miscella refining process for edible oils (2). E. M. James favorably reported on miscella refining in April 1957 in a paper comparing various refining methods (10). An acetone miscella refining process was described in the March 1961 J.A.O.C.S. (15). The advantages of lighter color and greater yields of excellent quality finished oil per ton of source material are real and demonstrable when oil is immediately miscella refined subsequent to solve extraction with the exclusion of air and light (2).

This report presents plant refining data comparing four different refining processes operating on cottonseed oil of moderately high and very low free fatty acid content. The refining methods compared are Ranchers Miscella, Low Loss, Modified Soda Ash, and Sanbra. (Sanbra is the Brazilian affiliate of Bunge.)

Description of Refining Processes

Ranchers Miscella Refining Process actually starts with the cooking of the meats and consists of the following steps: 1) Conditioning meats to contain 10–12% moisture at cooker discharge; 2) adding granular soda ash to the cooked meats to control the F.F.A. of the crude oil within desired limits (3); 3) batching crude 50% miscella in make-up tanks. (Two tanks make continuous operation possible.) 4) Continuously adding 8° to 20° Bé caustic soda through a rotometer into the suction side of the single crude miscella pump; 5) intimately contracting the dilute caustic with the crude miscella in an homogenizer (4); 6) heating the miscella to cause the soapstock to melt; 7) cooling the miscella to form a two-phase system for centrifugal separation (5); 8) separation of refined miscella and soapstock in vapor tight tubular bowl centrifuges. 9) Soapstock containing approximately 15% by weight of hexane may be desolventized in commercially available equipment and subsequently processed as ordinary caustic soapstock, or if the F.F.A. of the crude oil does not exceed 3% and economic conditions warrant, it may be added to the solvent-wet meal from the extractor with decidedly beneficial results to the quality of the meal (9). 10) The refined miscella may be contacted with a soap removing acid wash (6) or, in some instances, filtering through diatomaceous earth in a totally enclosed filer is preferred to water washing. Oils miscella refined according to the above procedure are very light in color. If bleaching is desired, bleaching earth can be substituted for the diatomaceous earth in the filter press and colors as light as required can be obtained with virtually no loss of oil in the filter clay. 11) If winterization is desired, this can be very effectively done in solvent at this stage of processing. Continuous separation of the stearine in valve operated disk type centrifuge gives about 87% yield of 20 hr. cold test cottonseed salad oil and 13% of 73 Iodine Value stearine. 12) Solvent is recovered in conventional equipment with the decided advantage that the distillation equipment operating on refined miscella never has to be cleaned. Ranchers Miscella Refinery and winterizer are preferably located in the solvent extraction plant so that the same operator(s) control all phases of the solvent extraction, refining, winterizing, solvent recovery, and deodorization processes.

The Low Loss process is a two stage refining process usually followed by double water washing to remove soap. The crude oil is first conditioned by admixture with 0.1% of citric or orthophosphoric acid. In the neutralization stage the conditioned oil is heated to 150°F and then a stoichiometric amount of caustic soda is added to the oil and the resultant soapstock