

THE SPECTROMETRIC EXAMINATION OF CERTAIN FIXED OILS AS A MEANS OF IDENTIFICATION.

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IN view of the conflicting statements made by Allen (*Comm. Organic Analysis*, Third Edition, II., p. 26), by Lewkowitsch (*Chemical Analysis of Oils, etc.*, Second Edition, p. 113), and by Doumer and Thibaut (*Corps Gras Industrielles*), it is obvious that any spectroscopic examination of any fixed oil exhibiting absorption bands is untrustworthy if reliance be placed upon the presence, or absence, of such phenomena for diagnostic purposes; and, as several fixed oils do not yield any absorption bands at all, simple spectroscopic examination alone would appear practically valueless as a means of identification. From what has been accomplished so far the only use of the spectroscope would seem to be for the purpose of placing an oil in a particular class—a waste of time so far as analytical procedure is concerned.

The observations recorded from my investigations are not proffered as conclusive, as, obviously, repeated examinations of similar oils from dissimilar sources are requisite before a table of definite limits of absorption or the ranges of visibility of the spectra of fixed oils could be accepted as infallible. Such a table, if free from error, would doubtless assist in the speedy identification of a fixed oil because it would prove discriminative.

With the foregoing reservation, my observations tend to show that dissimilar oils exhibit dissimilar limits of visibility under similar conditions, whilst oils of the same kind show practically identical spectra as regards length—that is, in the extent of the visibility of their spectra—under like conditions. Herein lies the true value of Allen's remark, that "no oils of animal origin give definite absorption bands, the spectrum being merely obscured at the more refrangible end."

METHOD.—The instrument used was a Browning's Student's Spectroscope fitted with a $1\frac{1}{4}$ -inch dense prism and provided with an arc of 100° divided into thirds of

a degree, having a vernier and lens, thus permitting angular measurements of the position of the axis of the telescope to be made.

The readings were taken of such angular measurements by bringing the telescope into such a position that one of the cross wires in the eye-piece, when in a vertical position, coincided with the extreme edge of the visible spectrum, so that on one side was the barely visible limit of the spectrum and on the other obscurity; or in the case of an absorption band, when the band was sufficiently wide to be conveniently measured, by bringing the wire into coincidence with the extreme edges of the band alternately. If the bands were not of such a breadth as to permit of this, the wire was brought into apparent superimposition; in each instance the reading on the scale of the arc was noted.

Measured in this manner, the length of the visible spectrum of white light was found to occupy a segment of the arc, beginning at the red end at 43° and ending at the violet at 47.6° . The range of the spectrum was thus 4.6° . The position of the sodium, or D line, was experimentally ascertained to be precisely at 44.3° , corresponding to division 50 on Bunsen's scale.

The apparatus consisted of dull black metal troughs of various lengths (usually 3 or 6 inches), having a window of clear white glass at either end. The window intended for use near the slit of the spectroscope was surrounded by a collar into which the collimator-tube of the instrument could be inserted, and on the end of the trough, remote from the spectroscope, a box-like attachment was constructed to receive the source of light.

The trough was filled with the particular oil at 30° C. to 40° C., and covered with a dull black lid, and the spectroscope placed in position after the small reflecting prism had been swung aside. From the opposite end a beam of light was transmitted through the oil from a metallic filamented $\frac{1}{2}$ -watt electric bulb of the gas-filled type (50 c.p.), and the slit of the spectroscope was suitably adjusted. As the observations were made in daylight the prism of the instrument was covered with a black cloth.

Diagrams of spectra made from the results obtained have shown that both the limits of visibility and the width of an absorption band, and in some measure its intensity, bear a relation to the horizontal thickness of the oil through which white light is transmitted.

In practice, some difficulty arises in precisely determining the edge of an absorption band, because the absorption becomes less towards the edge, which is therefore not sharply defined, but shaded off to a limit at which absorption is not detectable. Small differences due to this cause, however, are not so great as the differences, in most instances, of the extent of visibility of the spectra of oils of different nature which I have examined.

It would thus appear to be of no use merely to state the width of any absorption bands appearing in the spectrum of an oil, and if the breadth of a band be measured it should be connoted with the thickness of oil through which the light passes before entering the spectroscope. In view, however, of the untrustworthy evidence afforded by such bands too much reliance should not be placed either on their width or their presence or absence.

HOMOGENEOUS LIGHT.—The effect of passing light as nearly as possible homo-

geneous through the various oils was tried by interposing a red glass screen between the source of white light and the oil.

The visibility of the spectrum given by the screen itself ranged from 43.5° in the red to 44.3° in the yellow. It thus filtered out the whole of the violet, indigo, blue, green, and most of the yellow rays from white light, and permitted light very nearly homogeneous to penetrate the oil.

As was probably to be expected, in the case of those oils the spectra of which exceeded in visibility the spectrum of the screen, the spectrum obtained was that of the screen only.

Similarly, in the case of a mixture of two different oils yielding spectra with visibilities differing in extent, the spectrum observed when white light is passed through the mixture is (excluding any absorption bands due to chromogenetic causes in either oil) that of the oil giving the spectrum of the less extensive visibility, provided the limits of visibility at both ends come within the limits of visibility of the spectrum from the oil giving the more extended spectrum. Whether this holds good for an admixture of a very small amount of one oil with another remains yet to be determined.

SPECTROMETRIC CHARACTERISTICS.

Oil.	Three Inches of Oil used.			Six Inches of Oil used.		
	Visibility of Spectrum in the Red ends at—	Visibility of Spectrum in the Blue ends at—	Approximate Extent of Visibility.	Visibility of Spectrum in the Red ends at—	Visibility of Spectrum in the Blue ends at—	Approximate Extent of Visibility.
Almond	43°	47.3°	4.3°	43°	47°	4°
Arachis	43.3°	45.6°	2.3°	43.6°	45.3°	1.7°
Castor (East Indian)	Slightly varies about 43.2°	45 to 45.3°	2 to 2.3°	Six inches not suitable for examination		
Coconut	43.28°	47.3°	4.02°	43.3°	46.6°	3.3°
Colza (2 inches of oil)	43.3°	44.6°	1.3°	Six inches not suitable for examination		
Cotton seed (English refined)	43°	46.6°	3.6°	43°	45.6°	2.6°
Linseed, raw	Slight	45°	2.0°	Slight	44.6°	1.6°
Linseed, boiled ...	43.3°	44.3°	1.3°	43°	44.3°	1.3°
Neatsfoot	43.3°	45.64°	2.34°	43.6°	44.34°	About 0.74 , under 1°
Olive	Nil	45.3°	2.3°	43.16°	45.16°	2°
Sesame	43.16°	45.6°	2.46°	43.3°	45°	1.7°

CONCLUSION.—From the experimental data obtained it seems evident that careful spectrometric observations afford a quick and ready means of identifying a fixed oil, at any rate in the case of those specified.

The above table indicates the spectrometric characteristics of the oils examined,

from which it will be noticed the variations in the extent of visibility are most marked at the blue end of the spectrum, the limits of visibility at the red end not greatly varying.

It will also be seen that the lengths of the visible spectra are mostly different.

DISCUSSION.

Mr. H. C. REYNARD said he would like Mr. Gardner to give some idea of the effect of the age of the seed from which the oil is extracted on the absorption spectrum, as there seemed to be more difference in the absorption spectrum of American "butter oil," prepared from fresh cottonseed, than in that of oil from the kind of seed we are accustomed to get in England. He considered that no amount of refining would give oil, from the latter seed, of so good a colour as the American oil. He feared that as a means of diagnosis of oil the method described by the author was likely to be too much affected by the method of refining and the source of the oil, although, judging by the amount of data given in the paper, probably the writer had already studied this question.

Mr. BOLTON said that, while he was not impressed by spectrometric methods as an analyst's weapon, the readings might prove useful as a manufacturer's method of sorting oils. The data given, however, were most valuable.

Mr. CHAPMAN asked for information as to what the absorption spectrum was really due. He inquired if certain constants were peculiar to certain oils, in which case the test might become of diagnostic value—apart from the other colour, which was, to some extent, accidental. He wondered if the speaker had examined tung oil.

Mr. GARDNER, in his reply, said that Mr. Reynard's point was, perhaps, the weakness of the method. A good deal of cottonseed oil was obtainable from India, the examples dealt with in the paper, however, being imported English refined oils. Undoubtedly the process of refining removed the chromogenetic principle, and colouring matters were rather a cause of absorption bands than otherwise. The colour which remained in the oil was dependent on clarifying, as would be realised on comparison with the figures given (in the charts) for neatsfoot oil. The absorption spectrum bore no relation to the constituents of the oil.

