(7) Collenberg and Bakke, *Z. anal. Chem.*, **63**, 229 (1923).
(8) Cushman, J. Ind. Eng. Chem., **10**, 380 (1918).
(9) Fales, "Inorganic Quantitative Analysis," p. 351 (1925).
(10) Fleyscher, *J. Am. Chem. Soc.*, **46**, 2725 (1924).
(11) Gooch and Blake, *Am. J. Sci.*, [4] **14**, 287 (1902).
(12) Groschuss, *Z. anorg. allgem. Chem.*, **103**, 186 (1918).
(13) Gruener, *Am. J. Sci.*, [3] **46**, 206 (1893).
(14) Hale, *Ibid.*, [4] **13**, 379 (1902).
(15) Hale, *J. Am. Chem. Soc.*, **24**, 828 (1902).
(16) Hillebrand and Lundell, "Applied Inorganic Analysis," p. 228 (1929).
(17) Jamieson, "Volumetric Iodate Methods," p. 12 (1926).
(18) Jungmichl and Hackl, *Melliand's Textilber.*, **7**, 850 (1926); *C. A.*, **21**, 545 (1927).
(19) Kessler, *Z. anal. Chem.*, **2**, 386 (1863).
(20) Knop, *Ibid.*, **63**, 81 (1923).
(21) Knop, *Ibid.*, **63**, 96 (1923).
(22) Koenig, *Chimie & industrie*, Spec. No., May, 1924; *C. A.*, **18**, 3332 (1924).
(23) Kolthoff, *Rec. trav. chim.*, **43**, 798 (1924); *C. A.*, **19**, 450 (1925).
(24) Kolthoff, "Volumetric Analysis," Vol. II, pp. 305, 410, 464 (1929).
(25) Lang, *Z. anorg. allgem. Chem.*, **142**, 229, 242 (1925).
(26) Low, "Technical Methods of Ore Analysis."
(27) Lutz, *Z. anorg. Chem.*, **49**, 338 (1906).
(28) Manchot and Oberhauser, *Z. anorg. allgem. Chem.*, **139**, 45 (1926).
(29) McMillan and Easton, *J. Soc. Chem. Ind.*, **46** 472 (1927).
(30) McNabb and Wagner, Ind. Eng. Chem., Anal. Ed., **1**, 32 (1929).
(31) Metzl, *Z. anorg. Chem.*, **48**, 156 (1906).
(32) Mohr, "Lehrbuch der Titriermethode," p. 261 (1862).
(33) Nakosono and Inoko, *J. Chem. Soc. Japan*, **47**, 20 (1926); *C. A.*, **20**, 3662 (1906).
(34) Rowell, *J. Soc. Chem. Ind.*, **25**, 1181 (1906).
(35) St. Györy, *Z. anal. Chem.*, **32**, 415 (1893).
(36) Scott, "Standard Methods of Chemical Analysis," p. 25 (1922).
(37) Sutton, "Volumetric Analysis," p. 153 (1924).
(38) Treadwell-Hall, "Analytical Chemistry," Vol. II, p. 209 (1924).
(39) U. S. Army Ordnance Dept., *Spec.* **50-11-14**, 3 (1923).
(40) Weller, *Ann.*, **213**, 364 (1882).
(41) Willard and McAlpine, *J. Am. Chem. Soc.*, **43**, 797 (1921).
(42) Willard and Young, *Ibid.*, **50**, 1376 (1928).
(43) Winkler, *Bull. soc. chim. Belg.*, **36**, 491 (1929); *C. A.*, **22**, 40 (1928).
(44) Zintl and Wattenberg, *Ber.*, **56**, 472 (1923).

Fluorescence of Olive Oil under Ultra-Violet Light[1]

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A study has been made of the fluorescence of olive oils under ultra-violet light to see if it could be used as a positive test for determining admixtures of refined and virgin oils. All pure virgin oils were found to exhibit a yellow fluorescence under ultra-violet light, while all refined oils show a blue fluorescence. By this means adulterations of as little as 5 per cent refined oil in a virgin oil can be detected.

The spectrum analysis of virgin olive oils shows a characteristic red band which is lacking in refined oils, but may be approximated by the addition of chlorophyll. The fluorescence of an oil is independent of its chlorophyll content.

A study of the effect of added carotene and annatto showed that the yellow fluorescence of the virgin oil could be obtained with oils adulterated with refined oil. The addition of annatto could be readily detected chemically, but not the carotene. The carotene content is believed to be directly responsible for the yellow fluorescence of a virgin oil.

At THE present time one rarely finds an olive oil that has been adulterated with sesame, cottonseed, or other foreign oil. However, the number of pure, virgin olive oils that are adulterated with cheaper, refined olive oil is surprising. Tests have been made in this laboratory on all the leading brands of olive oil of this country, and it has been found that over 40 per cent of the so-called pure, unadulterated virgin olive oils are falsely labeled—containing from 25 to 100 per cent refined oil.

Since the preliminary work on this subject in 1925 there have appeared a number of articles on the fluorescence of oils under the ultra-violet light. The chief purpose of this investigation was, therefore, to see if this phenomenon of fluorescence could be used as a positive test for determining admixtures of refined in virgin olive oils. The work has been divided into two parts: first, the determination of the characteristic fluorescence of virgin and refined olive oils; secondly, the attempt to approximate with a refined oil the fluorescence of a virgin oil.

It is to be understood that, unless stated to the contrary, all oils mentioned in this article are olive oils.

Determination of Fluorescence

Procedure—The experimental procedure consisted in observing the oils under the light from a quartz-mercury arc lamp. An air-cooled lamp was used in conjunction with a Corning ultra-violet filter fitted so as to obtain horizontal radiation only. Observation of the samples was facilitated by working in a dark room.

The oil samples were placed in Pyrex test tubes of 15 mm. diameter, and the tubes were placed vertically 25 cm. from the Corning filter. Test tubes were used because they facilitated observation. Too great a thickness of oil made it very difficult and even impossible to observe slight differences in fluorescence. However, similar results may be obtained from quartz, sodium-glass, or flint-glass tubes. The fluorescence of each oil was then observed against a white and a black background. The black background was found to be best for observing slight variations in degree of fluorescence. Colored backgrounds proved impractical and impaired observation.

Results—Table I shows the fluorescence of the oils tested. In the first series are virgin olive oils of known history. Over fifty samples, representing the principal olive-oil producing districts of the Mediterranean, were examined, each one showing the characteristic yellow fluorescence of a virgin oil. It was also noted that oils from different localities did not vary greatly in fluorescence.

The Bureau of Standards (*1*) claims that California virgin oils will not always give a yellow fluorescence. A partial list of some of the California virgin oils examined is given in Table I. It can be seen that against a white background the majority of these oils give a deep yellow fluorescence which shows up orange against a black background. This compares with oils 11 and 12, which are imported virgin oils of the second pressing. Sample 7, labeled "virgin oil," gave a blue fluorescence which was comparable with sample 10, an oil known to be of the second pressing and heated during the process. The California process of extraction of oil involves four pressings. To the third and fourth heat is applied, and after the oil is extracted all four pressings are generally

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mixed together. Oil from the first pressing will usually show a pure, virgin fluorescence, while the second pressing will show deep yellow to orange. In the third and fourth pressings of the oil the action of heat partially refines it and is the cause of the blue fluorescence.

The fluorescence of refined oils is also given in Table I. By "French-refined" is meant the oil of the third and fourth pressings subjected to the ordinary methods of refining and deodorizing. "Pulp-refined" refers to oil that is extracted from the hulls of the olives by carbon disulfide or trichloroethylene and subsequently refined or deodorized in the usual manner. The fluorescence of the pulp-refined oil is seen to be a deeper blue than that of the French-refined oil.

Admixtures of refined and virgin oils vary in fluorescence according to the percentage of the oils in the mixture.

Table I—Fluorescence of Various Virgin and Refined Olive Oils

Sample	Type	Fluorescence: White background	Fluorescence: Black background
		VIRGIN OILS	
1	Andria	Canary yellow	Yellow with faint orange cast
2	Sousse	Canary yellow	Yellow with faint orange cast
3	Sousse	Canary yellow	Yellow with faint orange cast
4	Andria	Canary yellow	Yellow with faint orange cast
5	Sfax	Canary yellow	Yellow with faint orange cast
6	Sfax	Canary yellow	Yellow with faint orange cast
7	Aragon	Yellow	Orange
8	Bitonto	Yellow	Yellow
9	Sousse	Yellow	Faint orange
10	Riviera	Canary yellow	Yellow
11	Sousse	Canary yellow	Yellow
12	Sfax	Lemon yellow	Yellow
13	Sfax	Canary yellow	Yellow
14	Sfax	Canary yellow	Faint orange
		SO-CALLED VIRGIN CALIFORNIA OILS	
1	California	Deep yellow	Yellow with orange cast
2	California	Canary yellow	Yellow
3	California	Orange	Deep orange
4	California	Deep yellow	Orange
5	California	Yellow	Yellow with bluish tint
6	California	Pale orange	Orange
7	California	Blue	Blue
8	California	Yellow	Orange
9	California, 1st pressing	Yellow	Yellow with bluish cast
10	California, 2nd pressing	Blue	Blue
11	Sousse, 2nd pressing	Deep yellow	Pale orange
12	Sfax, 2nd pressing	Pale orange	Orange
		REFINED OILS	
1	French-refined	Sky blue	Sky blue
2	Pulp-refined	Sky blue	Deep blue
3	Cottonseed	Blue	Blue
4	Sesame	Blue	Blue
5	Peanut	Blue	Blue
		MIXTURES OF VIRGIN AND REFINED OILS	
6	90% Virgin Sousse, 10% French refined	Milky yellow	Bluish yellow
7	50% Virgin Sousse, 50% French refined	Milky blue	Milky blue
8	25% Virgin Sousse, 75% French refined	Blue	Blue

It is evident from the above results that every virgin olive oil will give a yellow to faint orange fluorescence under filtered ultra-violet light. On the other hand, every refined olive oil, no matter what the process of refining, will give the characteristic bright blue fluorescence. Admixtures of refined in virgin oil show a blue fluorescence that is directly proportional to the percentage of refined oil present. Ten per cent refined oil can be readily detected, and the experienced observer can detect as little as 4 per cent refined oil in virgin oil. Below this amount the blue fluorescence of the refined oil is completely masked by the yellow fluorescence of the virgin oil. By making up a series of controls, starting with 100 per cent virgin and adding refined oil in 10 per cent quantities up to 100 per cent refined, it is very easy to estimate plus or minus 2 per cent the quantity of a refined and virgin oil in a mixture.

Effect of Adding Chlorophyll

Stratta and Mangini (*3*) have shown that the spectrum of fluorescence of chlorophyll shows a band situated near the region of 620 to 680 $\mu\mu$ corresponding to that principal band of the absorption spectrum described by Willstätter (*4*). A solution of chlorophyll generally presents an intense red coloration in the ultra-violet region.

Nasini and De Cori (*2*) show that a refined olive oil does not have in its spectrum the characteristic red band of a virgin oil. Carotene in solution exhibits a yellow fluorescence similar to a virgin oil. Small quantities of chlorophyll and carotene added to a refined oil brought back the characteristic red band to the spectrum and also masked the blue fluorescence of the refined oil.

By comparing the intensities of the red band in the spectrum, the percentage of adulteration of a virgin oil by a refined may be detected, even in amounts of 1 per cent. However, if chlorophyll has been added, the spectrum analysis cannot be relied upon.

In lieu of this, the following experiments were made in order to see how chlorophyll would react in masking the blue fluorescence of a refined oil. Five samples of commercial chlorophyll of unknown source and one sample of commercial chlorophyll of known source were obtained.

Note—Nasini and De Cori state that all commercial chlorophyll will not serve to mask the properties of a refined oil. This sample was extracted by the method they prescribe—i. e., extraction from leaves of *Urticae Dioica L* using methanol and petroleum ether and not heating above 30° C.

In addition, a fairly pure chlorophyll was obtained by extracting spinach with methanol and petroleum ether and evaporating off the solvents.

Solutions of these chlorophylls ranging from 0.001 to 2 per cent were made in alcohol, benzine, chloroform, ether, acetone, carbon disulfide, and carbon tetrachloride. These solutions did not give a yellow or red fluorescence, but presented in dilution a rather greenish cast. When the concentration reached 0.5 per cent, the solution under ultraviolet light appeared a grayish brown, and in daylight a dark emerald green. Addition of a few drops of these chlorophyll solutions to a refined oil caused no change in fluorescence. Larger quantities changed the color of the fluorescence to green; and after adding an excess of chlorophyll the fluorescence changed to a grayish brown, while the oil assumed an emerald green color. Identical results were obtained from each kind of chlorophyll, whether added by itself or in solution in one of the solvents. Heating to drive off the solvent served to intensify the grayish brown fluorescence.

This leads to the conclusion that the characteristic yellow fluorescence of a virgin oil under ultra-violet light is dependent, not upon the chlorophyll content, but upon the yellow coloring matter present.

Effect of Adding Carotene

Carotene (imported, made from palm oil)[2] was dissolved in petroleum ether, filtered, and evaporated to dryness to repurify. This, in solution in petroleum ether, exhibited a yellow fluorescence similar to that of a virgin oil. Addition of this dissolved carotene to a 100 per cent refined oil gave a yellow fluorescence with a slight bluish cast, approximating an 80 per cent virgin and 20 per cent refined oil mixture. After heating to drive off the ether, the fluorescence remained the same. Addition of an excess of carotene approximated the fluorescence of a 90 per cent virgin and 10 per cent refined oil. A mixture of 50 per cent virgin and 50 per cent refined can be made to resemble 90 per cent virgin and 10 per cent refined. A 10 per cent addition of refined oil to 90 per cent virgin could not be detected after carotene had been added. It would seem, then, a simple matter to imitate a virgin oil merely by adding the requisite amount of carotene to a refined oil. This can readily be done, but the cost of added carotene would, at present, exceed the difference in cost between refined and virgin oil.

[2] Supplied by courtesy of L. M. Roeg.

Effect of Adding Annatto

Annatto, oil-soluble, has an orange fluorescence under ultra-violet light. The addition of 2 drops of annatto solution to 10 cc. of a 100 per cent refined oil colored it a slightly darker shade of yellow than that of the average virgin oil. Under the ultra-violet light against a white background there was practically no difference between this treated refined oil and a pure virgin oil; but when viewed against a black background the virgin oil maintained its yellow fluorescence while the refined oil plus annatto showed the characteristic appearance of a virgin oil diluted with 10 per cent refined. A mixture of 50 per cent virgin, 50 per cent refined plus annatto can be made to approximate a virgin oil that contains only 5 per cent added refined oil.

There was no difference in the fluorescence of a virgin oil and a mixture of 75 per cent virgin and 25 per cent refined to which annatto had been added; the orange fluorescence of the annatto completely covered up the light blue fluorescence of the mixture and gave to the whole a yellow fluorescence identical with that of a virgin oil. Annatto, however, can be tested for chemically, and so its addition to an oil can readily be detected.

Color Readings

The building up of the yellow fluorescence by the addition of carotene or annatto to a refined oil is conclusive evidence that the virgin fluorescence is directly dependent on the percentage of yellow coloring matter present. To substantiate this, color readings were made on virgin and refined oils, using standard Lovibond color glasses. The results are given in Table II.

Table II—Average Lovibond Color Readings on Virgin and Refined Oils

Oil Samples	No. of Oils Tested	Yellow	Red	Blue
Authentic virgin olive oils	28	60.51	4.71	2.10
French refined olive oils	5	40.00	1.28	0.00
French refined plus sufficient annatto to give yellow fluorescence	5	60.00	6.00	0.00
French refined plus annatto plus chlorophyll	5	60.00	6.00	1.78

Effect of Solvents

It was also found that the solvents for oils would reduce the blue fluorescence. Carbon disulfide, carbon tetrachloride, chloroform, ether, and acetone by themselves are not fluorescent. On their addition to a refined oil the bluish fluorescence was cut down and there was given to a 100 per cent refined oil a fluorescence approximating that of a 70 per cent virgin and 30 per cent refined mixture; but the concentration of the solvent was so high (30 per cent) that it materially changed the viscosity of the oil.

After heating to drive off the solvent, the original blue fluorescence of the refined oil was again obtained. If as little as 0.5 per cent of the adulterant is left in the oil, it can readily be detected by taste, and when present in this small proportion it does not in any way cover up the blue fluorescence of the refined oil.

Conclusions

1—All pure virgin oils exhibit a yellow fluorescence under ultra-violet light, while all refined oils show a characteristic blue fluorescence.

2—By means of fluorescence adulterations of 5 per cent refined oil in a virgin oil can be detected.

3—The fluorescence of California oils is due to the application of heat during the pressing and also to the extent to which the olives are pressed.

4—The spectrum analysis of virgin olive oils shows a characteristic red band at the region of 669 $\mu\mu$ which is lacking in refined oils, but may be approximated by the addition of chlorophyll to the oil.

5—The blue fluorescence of an oil is independent of its chlorophyll content.

6—The carotene content is directly responsible for the characteristic yellow fluorescence of a virgin oil, and the blue fluorescence of a refined oil is due to a decrease in content or to some chemical change brought about in the carotene during the refining process.

Literature Cited

(1) "Fluorescence as a Means of Detecting Admixtures of Refined in Unrefined Edible Olive Oils," Bur. Standards, *Tech. News Bull.* **127** (November, 1927).
(2) Nasini and De Cori, *Ann. chim. applicata*, **19**, 46 (1929).
(3) Stratta and Mangini, *Giorn. chim. ind. applicata*, **10**, 205 (1928).
(4) Willstätter und Stoll, "Untersuchungen über Chlorophyll," p. 169 (1913).

Magnetic Switches in Regulatory Circuits[1]

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Recent articles dealing with relays and thermostatic control circuits indicate that many chemists are unaware that standard electrical apparatus, which is both cheap and trouble-proof, may be used advantageously for regulatory circuits.

At the Pacific Experiment Station of the U. S. Bureau of Mines we have used for many years the combination of a standard 250-ohm telegraph relay and an alternating current magnetic switch for all electric circuits of this type. One such combination was in operation continuously for six years without interruption from trouble with contacts. The thermostat regulator, or other make-and-break device, operates the standard telegraph relay with an energizing current of 5 to 10 milliamperes. The contact mechanism of the relay in turn operates the magnetic switch. We have found very satisfactory the switch known as a G.E. CR7022-A3 magnetic switch. This switch may be connected directly to a 110-volt, 60-cycle line, through the relay contacts, as the energizing current is only 150 to 175 milliamperes. It is rated at 15 amperes capacity, and larger units are available. The contactor of the magnetic switch is U-shape, with contacts at each tip, and is therefore suitable either for opening and closing a circuit or for short-circuiting a section of a rheostat. As most thermostats are operated effectively only if the current is not completely opened but instead is charged slightly, the latter advantage alone justifies the use of this combination. The change from the open-circuit type of regulation to the current-increment type is accomplished simply by the reversal of the insulated and conductive points of the relay contacts.

The current-increment type of regulation is the only suitable one for heaters at high temperatures. The combination described has been used successfully in this laboratory for many types of electric tube and muffle furnaces.

The relay costs about $8 and the magnetic switch $4. Thus the combination is cheaper than other types of relays rebuilt to carry currents of sufficient size for heaters.

[1] Received May 16, 1930.