Rancidity Determinations

Calling Attention to a Possible Source of Error in the Kreis Test

BY WILMER C. POWICK*

IT has recently come to the writer's attention that in the examination of fats and oils for rancidity by means of the Kreis test with hydrochloric acid and phloroglucine, very misleading and puzzling results may be obtained through the use of hydrochloric acid containing nitrosyl chloride. While most acids examined, technical and c.p. alike, have been found to be satisfactory for the purpose, the technical acid prepared by one well-known manufacturer has been found to give the well-known ring test for nitric acid and an intense red color with phloroglucine, reacting in both instances in the same manner as pure hydrochloric acid to which a small amount of nitric acid has been added. It is well known, of course, that nitric acid in presence of concentrated hydrochloric acid passes to the form of nitrosyl chloride.

In spite of the strong "blank" test which this acid gave with phloroglucine, negative results were almost always obtained by its use in the Kreis test, even when the fats tested were known to be rancid. Evidently, while the acid was being shaken with the fat prior to the addition of phloroglucine, the nitrosyl chloride was in most cases completely removed by being added across the double bonds of the unsaturated fatty acids and was thus rendered unavailable for reaction with phloroglucine, but in case of rancid fats the removal of nitrosyl chloride was not complete until this compound had first destroyed the epihydrine aldehyde radical to which a truly positive Kreis test is due. That nitrosyl chloride is added across the double bond of oleic acid with the formation of the nitroso-chloride of elaidic acid, has been shown by Tilden and Forster (J. Chem. Soc. London, 65, 329); while direct experiment has shown that the epihydrine aldehyde radical in epihydrine aldehyde diethyl acetal is rapidly destroyed by hydrochloric acid containing nitrosyl chloride. In case of several fats with comparatively low iodine numbers, the reaction between the nitrosyl chloride and the unsaturated fatty acids appeared to proceed, as would be expected, more slowly, so that nitrosyl chloride was still present when the phloroglucine was added, as evidenced by the production of a red color of lower intensity than that obtained from the test on the acid alone. Spectroscopic examination of this color, naturally failed to show the absorption band centred at wave length 5400 A°, which is characteristic of the color similarly obtained from rancid fats by use of pure acid. Furthermore, even in case of these fats with comparatively low iodine number, the nitrosyl chloride could be removed from the impure acid by shaking the fat and acid together for a sufficient length of time—in

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some cases as much as ten minutes were required,—after which color formation was entirely lacking upon addition of phloroglucine.

It thus appears that no valid results can be obtained in the Kreis test if the acid, because of the presence of nitrosyl chloride, gives a "blank" test with phloroglucine. Under these conditions, rancid fats will generally appear to be sweet, while sweet fats may occasionally appear to be rancid unless the positive reactions be spectroscopically controlled. An illustration of the confusion that may result from this source was kindly brought to the author's attention by Mr. A. W. Putland, of Portsmouth, Va., who, as evidenced by Kreis tests performed with the acid in question, was consistently obtaining an apparently rancid hydrogenated product from apparently sweet non-hydrogenated cottonseed oils. Actually, the hydrogenated products examined by the writer showed no trace of rancidity when the Kreis test was performed with pure acid.

While the Kreis test affords a reliable means for detecting rancidity, or incipient rancidity in fats and oils, it must of course be used with circumspection. In the absence of spectroscopic control, as has elsewhere* been pointed out, positive tests obtained from cottonseed oils are not sufficient evidence of rancidity. It now develops that the test may be completely invalidated, in case of all fats and oils, positive and negative tests alike, by the use of an unsatisfactory reagent.

* Powick: Compounds Developed in Rancid Fats—Jour. Agric. Research Vol. XXVI., No. 8, pp. 336-338, November 24, 1923.

A Useful Addition to Laboratory Extraction Technique

BY PAUL L. MENAUL

The laboratory technique in the determination of oil in cottonseed meal samples appears so simple that no "stunt" could be added to insure greater precision. Yet a brief survey of the reports of the A. O. C. S. Meal Samples discloses a too wide variation in the reports of the oil content; a variation of 0.35% to 0.85% between extremes.

To the undersigned the best technique seemed to be to enfold the sample in a 12.5 cm filter paper, which is then enrolled in another 12.5 cm filter paper, placed in the extraction tube and extracted the required time. However carefully this is done, an appreciable amount of meal dust appears in the extract, varying with the fineness of the meal and the quality of the filter paper. It is rarely that a water clear extract can be obtained.

The author is using a most simple stunt in connection with this method, which invariably yields water clear extracts, and complete extraction of the oil.

This stunt is to moisten the mere lower tip of the outside paper with distilled water. The papers are so rolled that the outer filter paper extends about one half inch below the inner one containing the sample. This empty tip is dipped quickly in distilled water so that only the lower one quarter or one half inch is moistened. *The meal sample must not be moistened!* This moistened tip retains all the meal dust yet does not interfere with the oil extraction. It is also noteworthy that the cheapest filter papers serve as well as the best.