

crude ethoxide after filtering through surgical absorbent cotton. After reaction with more than the theoretical amount of palmitic acid and extracting the dried (at 45°) product with ether, the aluminum content was 4.8% as compared with the 5.1% already quoted. In a final experiment with dried benzene which had dissolved 77% of the crude ethoxide the product was dried in four portions at 25, 45, 55 and 75°. The crude material contained between 2.85 and 3.00% of aluminum and after hydrolysis with sulfuric acid yielded fatty acid determined by titration in alcoholic potash corresponding to from 78.96 to 94.84% of palmitic acid. These four products after extraction with sodium-dried ether contained, respectively, 5.38 and 4.43, 5.36 and 5.34, 5.29 and 5.20, 5.24 and 5.33% of aluminum, whereas aluminum tripalmitate would contain only 3.400% of aluminum. These results again indicate that not more than the dibasic palmitate is attained even under these unusually favorable conditions.

Our conclusion is that aluminum soaps are commonly a mixture of uncombined free fatty acid with either a monobasic or a mixture of mono- and dibasic soaps. Normal tribasic aluminum soaps have never been prepared even in completely anhydrous media.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD UNIVERSITY, CALIFORNIA

RECEIVED MAY 23, 1932
PUBLISHED AUGUST 5, 1932

[CONTRIBUTION FROM THE MEDICAL SCHOOL, UNIVERSITY OF OTAGO, NEW ZEALAND]

THE DETERMINATION OF IODINE IN BUTTERFAT

BY H. A. A. AITKEN

RECEIVED DECEMBER 12, 1931

PUBLISHED AUGUST 5, 1932

The estimation of iodine in carbonaceous materials such as oil or butter is generally regarded as the most difficult of all estimations of minute amounts of iodine in natural products. The most recent method that has been described is that of McClendon, Remington, von Kolnitz and Rufe,¹ in which melted butter (as much as 500 g. in one sample) was sprayed from an atomizer into a silica tube and burnt with a current of oxygen in the presence of a catalyst. This process obviates the difficulty inherent in the much simpler method of combustion with alkali, namely, that the low iodine content of the material necessitates so large a sample being taken for analysis that the use of an excess of potash is out of the question. This leads to loss of iodine, and in addition there is a pronounced tendency for the products of saponification of the butter to froth up during combustion in an uncontrollable fashion.

However, in the micro-titration method devised by the author for the

¹ J. F. McClendon, Roe E. Remington, Harry von Kolnitz and Redding Rufe, *THIS JOURNAL*, **52**, 541 (1930).

analysis of blood for iodine,² as little as 0.4 microgram of iodine in the sample suffices if the worker is content with a possible error of not more than 5%. When this method is applied to butter or butterfat (average iodine content about 20 microgram/kg.), a comparatively small sample of 25 g. will provide sufficient material for an analysis.

As a result it is possible to carry out a gentle combustion in the presence of an amount of caustic potash far in excess of that required to saponify the butter. Under these conditions, indeed, the process except in its final stages is better described as an alkali-fusion, the evolution of hydrocarbons from the melt taking place at a relatively low temperature. The iodide formed can be extracted readily and quantitatively from the resulting potassium carbonate and estimated immediately by titration. The method is a much more rapid one than the silica-tube method and probably gives more accurate results.

The procedure in actual practice is as follows: 25 g. of butter (or butterfat) is placed in a 20-cm. nickel basin and 20 cc. of 50% caustic potash is added, followed by 80 cc. of alcohol. All reagents and vessels used must be iodine-free. The butter is saponified by heating for an hour on the water-bath, and the contents of the basin are then evaporated gently to dryness on the sand-bath. The dry residue is now ignited below red heat over a gas-ring. The arrangement used to avoid overheating is shown in Fig. 1. The basin is set in a shallow iron dish about 15 cm. in diameter and 3.8 cm. deep, the depth being such that an air space intervenes between the bottom of the basin and the iron dish. This eliminates the possibility of local overheating. A trial is made with the basin empty and shaded from direct light to determine how strong a flame can be used without bringing the bottom of the basin to a glow. At this temperature the contents of the basin are found to form a melt from which hydrocarbons are evolved over a period of about three hours, the volume of the melt at the same time steadily diminishing. The process is accelerated by occasionally stirring with a nickel spatula set in a wooden handle, and distributing the material over the heated surface of the basin.

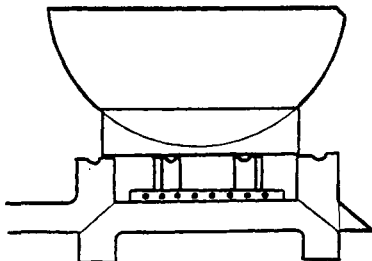


Fig. 1.

When evolution of gases has ceased, combustion is continued for a further half hour or more until a gray layer of potassium carbonate remains in the basin. The basin is cooled and the layer of salt washed down with a small amount of water, evaporated to dryness, and again ignited for half an hour. The residue is now taken up with about 150 cc. of water and filtered hot with gentle suction using a 10-cm. Büchner funnel and a 250-cc. filter flask. A fast pipet (about 50-cc.) can be used to transfer the liquid from the basin to the filter; the pipet is rinsed into the empty basin and this liquid is used to wash the precipitate. The filtrate and washings, which should be almost colorless, are now transferred to a clean basin and evaporated to dryness. The residue is ignited as before for a further quarter of an hour and allowed to cool.

Just sufficient half-saturated potassium carbonate solution (about 8 cc.) is now added to produce a smooth paste when rubbed into the residue by means of two stout

² H. A. A. Aitken, *Biochem. J.*, **24**, 1456 (1930).

glass rods with flattened ends. Formation of the paste may be assisted by the addition of a few cc. of 90% alcohol. About 25 cc. of 95% alcohol is added and stirred thoroughly into the paste. The extract is decanted into a 100-cc. nickel crucible with the aid of a thin glass rod, the lip of the basin being smeared with vaseline. The extraction is repeated two or three times, a total volume of about 75 cc. of alcohol being employed. If the paste has been made too thin it is an advantage to use absolute alcohol for the extraction; if it becomes too stiff, 90% alcohol is used.

The alcoholic extract with the addition of a little water is gently evaporated to dryness on the sand-bath. The residue of salts is rinsed down with a thin stream of water from a wash bottle, only a few cc. being employed, and the resulting solution is decanted into a 25-cc. nickel crucible. The process is repeated two or three times, a total of about 18 cc. of water being used. The contents of the small crucible after addition of about 10 drops of saturated potassium carbonate are evaporated carefully to dryness on the sand-bath and ignited for about five minutes by placing the crucible in a slightly larger one containing a few chips of pipe-clay to prevent actual contact and heating the outer crucible in a large non-luminous flame.

The residue is carefully moistened with a few drops of saturated potassium carbonate solution so as to form a paste as before when rubbed with two small glass rods. The alcoholic extraction is then carried out, this time with successive small amounts of about half a cc. of alcohol. The extracts are decanted into a titration tube, a particle of pumice is dropped in to initiate the boiling, the tube is suitably supported on the sand-bath and the contents are evaporated to dryness. (The titration tube is a tapering tube such as can be made from a centrifuge test-tube. A platinum wire is sealed into the bottom to ensure regular boiling.)

To the tube which now contains a very small residue of salt is added about 1 cc. of water and the resulting solution is acidified by adding three drops of 1% sulfuric acid from a dropping bottle. Three drops of fresh saturated bromine water are added, the solution is evaporated to a volume of about 0.3 cc. and cooled; a minute crystal of potassium iodide is added, and then a small drop of fresh starch solution. The iodine liberated is titrated in good diffuse light with *N*/100 thiosulfate from a micrometer screw buret.³ If the sample taken contains rather more than 0.4 microgram of iodine, the yellow color of free iodine will be discernible on adding the iodide, and the solution should then be titrated until nearly colorless before adding the starch.

Duplicate analyses by the above method generally agree within 2 to 5% depending on whether the sample has a high or a low iodine content. The reliability of the method has also been checked by testing the recovery of added amounts of iodine. Three identical 25-g. samples of a butter containing 45 micrograms of iodine per kg. were taken and to each of two samples before saponification was added 2 cc. of a solution containing 0.55 microgram of iodine per cc. The three samples were then analyzed with the following result

Sample 1	No iodine added.	Contained 1.09 micrograms
Sample 2	1.10 microgram added.	Contained 2.16 micrograms
Sample 3	1.10 microgram.	Contained 2.16 micrograms

Thus 1.07 or 97% of the iodine added was recovered.

The following are some recent values obtained for butterfats from different places in Otago, New Zealand.

³ H. A. A. Aitken, *Biochem. J.*, 25, 446 (1931).

Source.....	Dunedin	Highcliffe	Kokonga	Momona	Ranfurly
I ₂ content, microgram/kg.....	18	62	21	74	58

As pointed out by the American workers, analyses of butter are of questionable value in the mapping of iodine-efficiency areas on account of the increasing use of iodized dairy feeds and salt licks.

Summary

The iodine content of butterfat may be determined by igniting a relatively small sample with caustic potash, extracting the iodide from the resulting potassium carbonate with alcohol and estimating the iodine by micro-titration using a standard thiosulfate solution.

DUNEDIN, OTAGO, NEW ZEALAND

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, NATIONAL TSINGHUA UNIVERSITY]

ALLYL LEVULINATE AND ITS DERIVATIVES¹

BY PETER P. T. SAH AND TSU-SHENG MA

RECEIVED JANUARY 11, 1932

PUBLISHED AUGUST 5, 1932

A number of alkyl levulinates² were recently synthesized and studied. Allyl levulinate, representing an unsaturated ester of levulinic acid, has not been reported in the literature. We have successfully prepared this new ester in a very pure condition by direct esterification of levulinic acid³ with allyl alcohol,⁴ using hydrogen chloride as the catalyst. Apparently at low temperature the extent of addition of hydrogen chloride on the ethylene linkage was too slight to affect the yield and the purity of the product. We have further allowed chlorine or bromine to add on the new ester and found the addition products to be identical in physical properties with those obtained by direct esterification of levulinic acid with β,γ -dichloropropyl or β,γ -dibromopropyl alcohol.

To characterize these three new esters, their corresponding semicarbazones and phenylhydrazones were prepared by the usual methods. They were carefully purified and their melting points determined. The experimental details are hereby communicated.

¹ This paper is from a thesis presented by Tsu-Sheng Ma to the Faculty of National Tsinghua University in partial fulfilment of the requirements for the degree of Bachelor of Science, July 1, 1931.

² (a) Sah and Ma, *THIS JOURNAL*, **52**, 4880 (1930); (b) Schuette and Cowley, *ibid.*, **53**, 3485 (1931).

³ (a) Schuette and Sah, *ibid.*, **48**, 1394 (1926); (b) Thomas and Schuette, *ibid.*, **53**, 2324 (1931).

⁴ Kamm and Marvel. "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, pp. 15-19.