Determination of Citric Acid in Fats

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Abstract

The direct analysis of small amounts (2–50 ppm) of citric acid in refined glyceride oils and fats is described. Fat, containing citric acid, is titrated potentiometrically in a pyridine/acetone mixture with tetrabutylammonium hydroxide (TBAH). The method is relatively simple and rapid with an accuracy better than ±5%.

Introduction

OWING TO ITS COMPLEXING properties towards metals, citric acid is frequently used as an additive to oils and fats. It thus functions as a scavenger and chelates heavy metals, which will decrease their prooxidative abilities toward the oil or fat. In order to study the processing problems in connection with the use of citric acid, a quantitative analytical method with high accuracy and reproducibility was developed.

Several methods for the determination of small amounts of citric acid in biological materials have been described. Most of these methods are based on color reactions, viz., the pentabromoacetone method (1) and the so-called Fürth-Herrmann reaction (2). However there are few reports of methods for the determination of citric acid in oils and fats. With a micro method based on pentabromoacetone Buschbeck (3) found poor agreement when fatty matter was present, and he concluded that a necessary condition for the applicability of the method in such cases was to remove the oil, e.g., by extraction. Such a method has been described by Masuyama (4). Another procedure is reported by Choy et al. (5), based on the Fürth-Herrmann reaction and suitable for "oily" samples. However none of these methods has given sufficient quantitative accuracy in the 0–50 ppm range.

The direct titrimetric procedure which will be described in the following sections has been found to function satisfactorily after the problems with solvents and the electrode system were solved.

Experimental Procedures

Solvents

In pyridine, citric acid is protolyzed in two distinct steps: in the first, one proton is split off; and in the second, the two remaining. In the pH range of the second step, disturbances from "acidic impurities" were observed. At low citric acid levels the amounts of these disturbing compounds in proportion to the citric acid are so dominating that, in practice, only the first step can be used since this step is not influenced to any appreciable degree.

Pyridine (ACS spec.) is purified in the following way. After distillation between 114–117C, the solvent is shaken with 20 g/liter of fused potassium hydroxide, filtered, and thereafter redistilled. Pyridine purified in this manner has a low blank value, and the titration curve is well developed.

Acetone (ACS spec.) was used without further purification. From these solvents a mixture was made, consisting of two parts of pyridine and one part of acetone.

Apparatus

The measurements were performed with a Metrohm Potentiograph E 336. The volume of the burette was 5 ml. The burette tip and the storage bottle were connected by glass tubes with ball joints. The storage bottle was also provided with absorption tubes against moisture and carbon dioxide. The titration vessel was an ordinary 50-ml beaker (high form), which during the titration was covered with a lid that had the necessary holes for electrodes and burette tip.

Electrodes

The electrode system was composed of a Beckman glass electrode No. 4263 with a Metrohm sleeve type of calomel electrode EA 409 as reference electrode. The salt solution of the electrode consisted of ethylene diamine saturated with lithium chloride, according to Gran and Althin (6), in which agar had been slurried. The porous glass of the electrode had previously been plugged with this gel-like salt solution.

After completion of the measurements, the calomel electrode was cleaned and stored in a saturated potassium chloride solution; the bridge together with the glass electrode were placed in a 0.01 M ammonium acetate solution.

Titrant

Tetrabutylammonium hydroxide solution, 0.1 N in benzene/methanol 10:1 (BDH), was purified by passage through Amberlite IRA-400 in hydroxylic form, according to Cundiff and Markunas (8), and thereafter diluted with benzene/2-propanol 6:1 (7).

Titration Procedure

Ten grams of oil was weighed directly in the titration vessel and dissolved in 15 ml of pyridine/acetone (2:1).[1] The sample was titrated with TBAH-solution, standardized against salicylic acid[2] in 10 g of oil.

[1] Standards of citric acid were prepared by adding aliquot amounts of citric acid (p.a., Riedel-DeHaen AG), dissolved in pyridine to 10 g of oil.

[2] BDH, Analar, mw 138.13.

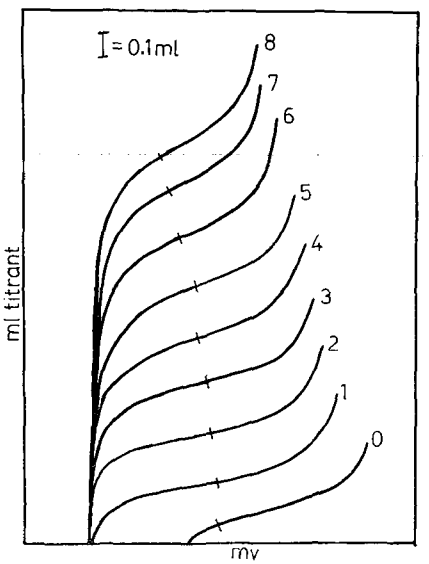

FIG. 1. Titration curves of citric acid in oil. O, blank value; 1–8, 2–15 ppm.

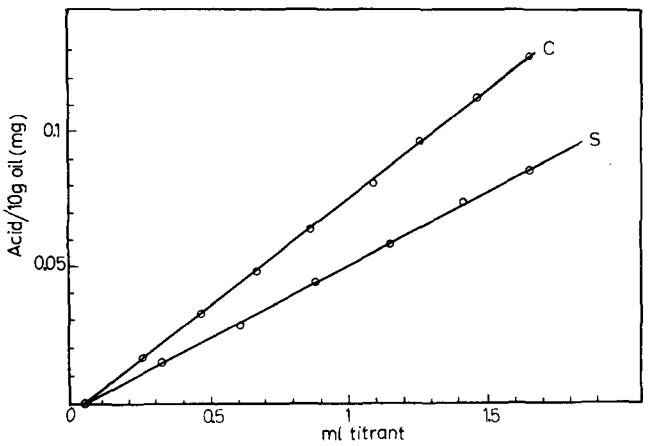

FIG. 2. The linear relationship of concentration and titrant in the 0–15 ppm range. C, citric acid; S, salicylic acid.

Normality range: $5 \cdot 10^{-4} - 10^{-3}$. The titration curve was automatically recorded on chart paper (Fig. 1). At the end of the titration the electrodes were thoroughly washed with trichloroethylene. Complications arising from oil films on the electrodes were thus eliminated (9).

Results and Discussion

Table I shows the results from four series of determinations. The figures are mean values of 10 titrations. As appears from Table I, the accuracy and reproducibility are satisfactory. The difference between Samples 1 and 2 depends on different normalities of the TBAH solution. The lower normality (Sample 2) is the most accurate, which is also to be expected. The linearity of the titration covers absolute values of citric acid at least up to 0.17 mg (Fig. 2). By lowering sample quantities, the concentration range can be extended with maintainance or even enhancement (owing to smaller proportions of fat) of accuracy, according to Table I.

TABLE I

Titration of Citric Acid in Oil

Sample	Citric acid theor. (ppm)	Citric acid found (ppm)	Standard deviation (ppm)	Relative deviation (%)
1	2.94	2.94	0.10	3.7
2	2.97	2.97	0.03	0.9
3	5.82	5.82	0.14	1.4
4	17.42	17.41	0.08	0.9

The titration curves in Fig. 1 show that the potential jumps gradually decrease with increasing volumes of titrant. This phenomenon is a solvent effect and leads to lower accuracy since the equivalence point will be more difficult to interpret. When titrations are performed within an expanded concentration range, it is advisable to change the normality of the TBAH solution or to change the sample weight in order to achieve maximum accuracy.

The method described is not specific for citric acid since other acids will also be titrated if they are protolyzed in the same pH range. However this limitation is of minor significance since the analysis, first of all, is intended to be used in connection with model investigations for which the accuracy is of primary importance. Besides, in refined oils and fats, there are normally no acidic components in the particular pH range. As to carboxylic acids, which of course are always present, it has been found that such acids (carbon length of 2 C and longer) have no influence on the determination.

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