

Determination of the Acidity of Oils Using Paraformaldehyde as a Thermometric End-Point Indicator

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Investigou-se a determinação da acidez de óleos graxos pela técnica da titulação termométrica catalítica empregando-se paraformaldeído como indicador termométrico de ponto final. Empregou-se como solvente da amostra uma mistura de tolueno e 2-propanol 1:1 (v/v) e como titulante uma solução de hidróxido de sódio 0.1 mol L⁻¹. O paraformaldeído, sendo insolúvel no solvente, não apresenta o inconveniente, que ocorre com outros indicadores de ponto final, de alterar a composição do solvente da amostra mudando suas propriedades, inclusive a solubilidade da amostra no mesmo. Este fato permite que a titulação seja realizada no mesmo meio em que é feita a titulação potenciométrica ou com indicador visual. Os resultados da aplicação do método à amostras de óleos graxos brutos e refinados são apresentados. O método proposto apresenta vantagens em relação a método potenciométrico em termos de rapidez e simplicidade.

The determination of the acidity of oils by catalytic thermometric titrimetry using paraformaldehyde as the thermometric end-point indicator was investigated. The sample solvent was a 1:1 (v/v) mixture of toluene and 2-propanol and the titrant was 0.1 mol L⁻¹ aqueous sodium hydroxide. Paraformaldehyde, being insoluble in the sample solvent, does not present the inconvenience of other indicators that change the properties of the solvent due to composition changes. The titration can therefore be done effectively in the same medium as the standard potentiometric and visual titration methods. The results of the application of the method to both non-refined and refined oils are presented herein. The proposed method has advantages in relation to the potentiometric method in terms of speed and simplicity.

Keywords: acidity index, fatty oil, catalytic thermometric titrimetry, paraformaldehyde

Introduction

The standard methods employed for the determination of acidity of oils are based either on titrimetry with visual indicators or, mainly in the case of coloured samples, on potentiometric titrimetry.¹ However visual indicators cannot be employed for coloured samples, and potentiometric titrimetry may be subject to the noxious effect of the sample solutions on the glass electrode. In this way, thermometric titrimetry, mainly catalytic thermometric titrimetry, which does not require severe precautions due to heat exchange with the environment, may be advantageous as an alternative method for the determination of the acidity of fatty oils. In addition, the apparatus involved in this technique is inexpensive and can easily be adapted to automation. In catalytic

thermometric titrimetry, the excess of titrant catalyses an exothermic or endothermic reaction and a temperature increase or decrease is used to locate the titration end-point.² In an earlier paper,³ we described the use of paraformaldehyde as an end-point indicator in the titration of acidic substances in aqueous solutions by thermometric titration with catalytic end-point detection. The decrease in temperature caused by the depolymerization of paraformaldehyde, catalysed by hydroxyl ions, was employed for the location of the end point of the titration. It is expected that paraformaldehyde, being insoluble in the sample solvent, will result in the determination of fatty acids by catalytic thermometric titrimetry in good agreement with those obtained by potentiometric and visual titrimetry in the referred solvent. This is expected because, in contrast to what happens in the case of other indicators, which are soluble in the sample solvent, in the paraformaldehyde case the indicator will not affect the

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properties of the titrand solvent nor the solubility of the sample. We report herein our results on the determination of the acidity of some crude and refined oils by catalytic thermometric titrimetry, employing paraformaldehyde as the end-point indicator. The titrations were performed in the same solvent mixture used in potentiometric and visual methods.

Experimental

Reagents

Sodium hydroxide, potassium hydrogen phthalate and propanol-2 were of analytical reagent grade. Toluene and paraformaldehyde were of laboratory-reagent grade. Paraformaldehyde was powdered and the resulting powder passed through a 100 mesh sieve (diameter of particles smaller than 0.149 mm). A 0.1 mol L⁻¹ sodium hydroxide solution was prepared and standardized with potassium hydrogen phthalate by the usual procedures.⁴ Crude castor, babassu, buriti and pequi oils and refined soya, corn, and sunflower oils were employed in this investigation. The crude oil samples have been obtained by heating the desired material (castor seeds, babassu almonds, or buriti and pequi pulps) with water and subsequent separation of the supernatant oil phase. The samples of refined oil, used in this work, were commercial samples obtained in the supermarket.

Apparatus

A motor-driven micrometer syringe, as described by Greenhow and Spencer,⁵ was employed to introduce the titrant at a constant delivery rate of 0.13 mL min⁻¹, both in potentiometric and thermometric titrations. In thermometric titrations the temperature changes were detected by locating the thermistor in one arm of a Wheatstone bridge and were recorded with a strip chart recorder, as described elsewhere.⁶ In potentiometric titrations, a pH probe containing both a glass and a reference electrode in the same body and, a model B375, Micronal pHmeter were employed.

Procedures

In visual titrations, the desired amount of oil, chosen in accordance with the A.O.C. S. method,¹ was dissolved in 125 mL of the solvent mixture (propanol-2 : toluene (1:1,v/v)), 2 mL of a 1% solution of phenolphthalein was added and the solution was titrated with aqueous 0.1 mol L⁻¹ NaOH. In both potentiometric and thermometric

titrations the desired amounts of oil were dissolved in the same solvent mixture, 25 mL in the case of the crude oils or 50 mL in the case of refined oils. However, the proportion between the oil mass and the solvent mixture volume, in both potentiometric and thermometric titrations, was the same as employed in the case of the visual titrations,¹ for each kind of oil. In the case of thermometric titrations, after the mixture of oil and sample solvent is homogenized in a unsilvered Dewar flask by using a magnetic stirrer, 0.6 g of paraformaldehyde is added. The titrant solution is added at a constant delivery rate of 0.13 mL min⁻¹ to the stirred solution. The end-point was taken where a tangent drawn through the main temperature decrease intersects the titration curve line at its high value. The volumes of the titrant obtained in the blank solution titration were subtracted from those corresponding to the titration of several samples. In the case of potentiometric titrations, except for the absence of paraformaldehyde, the same sample stirring, dissolution and titrant addition procedures were employed as in the thermometric titrations.

Results and Discussion

The titration of some samples of both crude and refined fatty oils by the technique of catalytic thermometric titrimetry, employing paraformaldehyde as an end-point thermometric indicator, was investigated. Crude castor, babassu, buriti and pequi oils and refined soya, corn, and sunflower oils were employed in this investigation. The thermometric titration curves obtained in these titrations are shown in Figure 1 and the results obtained in the determination of the acidity of the samples of crude and refined oils are presented in Table 1. In this table the results obtained for the acidity index by the proposed method are compared with those obtained by potentiometric titration, performed with continuous addition of titrant, and with the standard visual method. In the case of crude oils, with the exception of castor oil, the results obtained by catalytic thermometric titrimetry agree quite well with those obtained with either potentiometric or visual titrimetry. The large discrepancy in the case of castor oil, a highly coloured sample, may be related to the difficulty in observing the colour change of phenolphthalein at the end point of the visual titration. In the case of refined oils the results from catalytic thermometric titrimetry present a better agreement with those obtained by potentiometric titrimetry than those obtained by visual titrations. These larger discrepancies between the results from catalytic thermometric titrimetry and visual titrimetry may be explained by the assumption that some amount of the titrant is spent in the saponification of acylglycerides. This

Table 1. Results obtained for the acidity index of some samples of both non-refined and refined oils by catalytic thermometric titrimetry, potentiometry titrimetry and titration with a visual indicator

Oil Sample	Acidity Index ^a			Difference (%)	
	Thermometric Titrimetry ^b (T)	Potentiometric Titrimetry(P)	Visual Indicator(V)	(T-P)	(T-V)
Non-refined oil samples					
Castor oil	2.851 ± 0.021 ^c	2.844	3.134	+ 0.3	- 9.0
Babassu oil	0.947 ± 0.038 ^c	0.941	0.963	+ 0.7	- 1.7
Buriti oil	6.846 ± 0.052 ^c	7.251	7.040	- 5.5	- 2.8
Pequi oil	2.405 ± 0.017 ^c	2.294	2.501	+ 4.8	- 3.8
Refined oil samples					
Soya oil	0.624 ± 0.053 ^c	0.739	0.724	- 15.5	- 13.8
Corn oil	0.558 ± 0.092 ^c	0.516	0.961	+ 7.5	- 41.9
Sunflower oil	0.760 ± 0.055 ^c	0.740	1.005	+ 2.5	- 24.4

^a mg of KOH g⁻¹ of oil; ^b average of six determinations; ^c standard deviation; ^d colored sample.

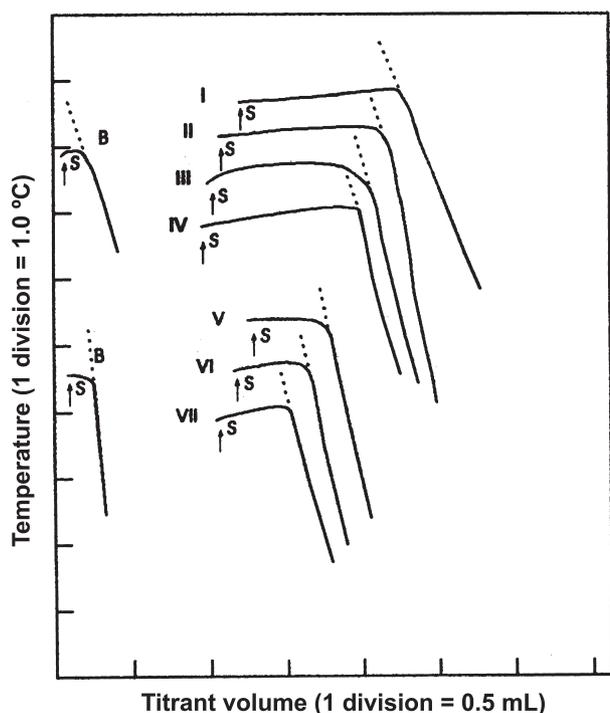


Figure 1. Thermometric titration curves obtained in the titration of oil samples. Sample solvent: (1:1, v/v) propanol-2 : toluene; Titrant: 0.1 mol L⁻¹ aqueous NaOH. Mass of paraformaldehyde (particle diameter < 0.149 mm): 0.6 g. I. non-refined castor oil (1.407 g); II. non-refined babassu oil (2.023 g); III. non-refined buriti oil (0.503 g); IV. non-refined pequi oil (1.502 g); V. refined soya oil (8.00 g); VI. refined corn oil (8.00 g); VII. refined sunflower oil (8.00 g); B. Blank solution. Sample solvent volume: 25 mL for non-refined oils and 50 mL for refined oils. S. start of titration.

is possible because, in the visual titration, the titrant is added manually at a lower delivery rate. This is corroborated by the fact that the difference between the results from potentiometric and visual titrimetry are of the same order of magnitude as the difference between thermometric and visual titrimetry. Thus, the method based on catalytic thermometric titrimetry, described here, may be chosen as an alternative method for the determination of the acidity of fatty oils. In fact it has advantages over both, the visual method, because it can be applied to coloured samples, and over the potentiometric method, in terms of speed of sample processing and simplicity.

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Received: October 23, 2001

Published on the web: August 19, 2002