Applications of automated thermometric titrimetry in routine process and quality control of fats and oils

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Titration

Summary

Modern laboratories involved in routine process and quality control of fats and oils demand high analytical productivity with minimum operator involvement. Automated thermometric titrimetry is well suited to the task. No electrical contact with titrating solutions is required, so samples can be titrated in a totally non-aqueous environment. The endpoint is determined automatically, not prone to operator bias and can be detected in highly colored or turbid solutions, or even in media containing suspended solids. The thermometric sensing probe requires no maintenance, special preparation, regeneration or calibration and can be stored dry between titrations.

Two determinations common in the analysis of fats and oils illustrate the versatility of the technique, namely the free fatty acid (FFA) content and the iodine value (IV). In both analyses, excellent agreement has been demonstrated with results obtained by official methods of analysis. The titrations are very fast, typically less than a minute in duration, and can be conducted using an automatic sample changer.

Introduction

Thermometric titrimetry is a technique nearly a century old, but only recently made practical for routine laboratory use by the advent of cheap, powerful computers and microprocessor-controlled instrumentation. In contrast to calorimetric techniques, the amount of analyte present is not determined from the temperature change. Instead, the technique relies on the rate of change of temperature in a stirred solution to which a titrant is added at a constant rate and reacted with the analyte in a sample. The titration endpoint or breakpoint is determined from an inflection in the temperature curve. There is no need to conduct the titration in special insulated vessels or in a thermostatically controlled environment. It is similar to other automated titration techniques, except that a thermometric probe is used to monitor the temperature of the titrating solution. There is no electrical contact with the titrating solution

A thermistor is used as the temperature sensing element of the thermometric probe.

Instrumentation

- 859 Titrotherm
- 800 Dosino with 10 mL burette
- 814 USB Sample Processor

Free fatty acid content

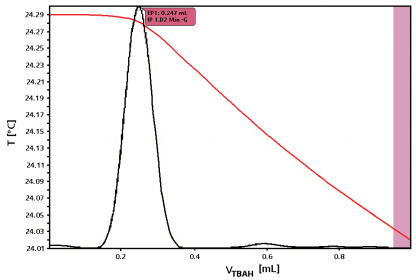
A previously described technique[1] has been found to be very suitable for adaptation to the automated thermometric titration of free fatty acids (FFA) in fats and oils. In the automated adaptation of the method, a sample of the oil or liquefied fat is weighed into a plastic titration cup and approximately 0.5 g of paraformaldehyde (PFO) is added. The cup is placed in the rack of an automatic sample changer and the titration program started. Under this program, the solvent mixture of toluene and 2-propanol is automatically added and the sample dissolved with stirring for a fixed time before titrant addition starts. The titrant is either 0.1 mol/L potassium hydroxide or 0.1 mol/L tetrabutylammonium hydroxide (TBAH) in 2-propanol, both standardized against A.R. benzoic acid. The endpoint is indicated by the base-catalyzed endothermic depolymerization of the paraformaldehyde, which causes the solution temperature to decline. The titration software detects the endpoint and stops the titration automatically. Titration data is sent to a user-designed spreadsheet for computation. The titration sequence finishes with a rinse in a suitable hydrocarbon solvent before the next sample is processed. Typical titration times range from 15 seconds to a minute.

FFA content of generic blended vegetable oils

The titrant is standardized against a solution of high-purity benzoic acid in 2-propanol, using the same solvent matrix as for the samples. FFA values down to at least 0.04% have been determined with 0.01 mol/L KOH in 2-propanol with good precision.

		Free fatty acid content [%][a]	
Sample no.	No. of determinations	Thermometric titration	Titration according to AOCS[b]
1	5	26.08 ± 0.08	25.70
2	2	0.263, 0.263	0.26
3	2	1.556, 1.558	1.54
4	2	8.33, 8.35	8.25
5	2	9.12, 9.10	9.00
6	2	31.72, 31.72	31.65

[a](w/w) as oleic acid
[b]manual titration performed independently by the supplier of the liquid samples according to AOCS Official Method Ca 5a-40



10 g sample, 0.5 g PFO and 35 mL of a 1:1 toluene : 2-propanol mixture (v/v) were titrated with 0.1 mol/L TBAH in 2-propanol. Determinations in triplicate yielded 0.046, 0.045 and 0.045% w/w FFA (as oleic acid). This titration was completed in 15 seconds.

Iodine value

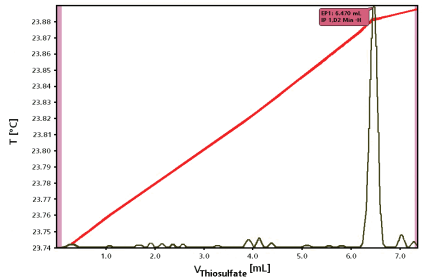
The iodine value (IV) is a measure of the total number of double bonds present in fats and oils. It is expressed as the «number of grams of iodine that will react with the double bonds in 100 grams of fats or oils». The determination is conducted by dissolving a weighed sample in a non-polar solvent such as cyclohexane, then adding glacial acetic acid. The double bonds are reacted with an excess of a solution of iodine monochloride in glacial acetic acid (Wijs' solution). Mercuric ions are added to accelerate the reaction. After completion of the reaction, the excess iodine monochloride is reacted with aqueous potassium iodide solution to form iodine, which is then titrated with standard sodium thiosulfate solution to an exothermic endpoint.

In the analyses reported here, the vegetable fat samples were gently melted and approximately 0.2 g accurately weighed into a tared titration vessel containing cyclohexane. Glacial acetic aid was then added, together with a small volume of mercuric acetate in glacial acetic acid solution. According to the titration program, Wijs' solution was added automatically. A programmed delay permitted reaction of the iodine monochloride with the fat before the potassium iodide solution was automatically added prior to thermometric titration of the iodine formed with standard thiosulfate solution

IV of vegetable fats

		Iodine value [g I_2/100 g sample]	
Sample no.	No. of determinations	Thermometric titration	Titration according to AOCS[a]
1	5	33.2 ± 0.08	35
2	5	50.5 ± 0.05	52
3	5	50.1 ± 0.13	50
4	5	54.9 ± 0.13	56
5	5	33.8 ± 0.09	35

[a]manual titration performed independently by the supplier of the fat samples



0.2 g sample was dissolved in 10 mL cyclohexane. Subsequently, 20 mL glacial acetic acid and 0.5 mL mercuric acetate solution were added. After the predosing of 6 mL of Wijs' solution and 300 seconds reaction time, the potassium iodide solution was added. Sodium thiosulfate was used as titrant. The reaction is exothermic.

References

1. M. J. D. Carneiro, M. A. Feres Júnior and O. E. S. Godinho, Determination of the acidity of oils using paraformaldehyde as a thermometric endpoint indicator, J. Braz. Chem. Soc. **13(5)**, 692-694 (2002).

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