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Short communication

Automated determination of acid value on fatty alcohols and fatty acids raw materials using potentiometric titration

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Introduction

The acid value (AV) is a common parameter in the specification of fats and oils (Ph.Eur. 2.5.1, current ed.). It is defined as the weight of potassium hydroxide (KOH) in mg needed to neutralize the organic acids present in 1 g of fat and it is a measure of the free fatty acids (FFA) in a sample of oil or fat indicates hydrolysis of triglycerides. Such reaction occurs by the action of lipase enzyme and it is and indicator of inadequate processing and storage conditions (i.e. high temperature and relative humidity). Different fat samples may contain varying amount of fatty acids. In addition, the fats often become rancid during storage and this rancidity is caused by chemical and enzymatic hydrolysis of fats into free acids and glycerol. The amount of free acids present, or acid value of fat is a useful parameter which gives an indication about the age and extent of its deterioration. The amount of free fatty acids can be determined by volumetric titration (manual), by which a sample in mixture of equal volumes of ethanol (96 per cent) and light petroleum is neutralized with potassium hydroxide (KOH) or sodium hydroxide (NaOH) using phenolphthalein indicator. (Ph.Eur. 2.5.1, current ed.). This is the recommended pharmacopeial procedure in many countries. But this manual method is attended with problems such as indicator error, the unclear color change in the transition range of the indicator may be a source of error. The volumetric titration has a lower rank of precision and accuracy due to this visual problem. To avoid the problem described, this method was optimized by automated titration using potentiometer. In the following we will discuss the automatic determination of the acid value of two raw materials and the comparison of results with the same method volumetric vs potentiometric.

Potentiometric titration

In a potentiometric titration (volumetric titration with potentiometric end-point determination) the end-point is determined by recording the variation of the potential difference between 2 electrodes (either 1 indicator electrode and 1 reference electrode, or a combined electrode) immersed in the solution to be examined as a function of the volume of titrant added. The end-point of the titration is reached when the maximum change in potential occurs in a plot of potential versus volume of titrant, and is expressed as the corresponding volume of titrant. Recording the first or second derivative curve can facilitate the determination of the end-point. (Pass and Sutcliffe, 1974).

Standardization

To apply this method, the first step is to standardize the titrant that will be used. The so-called titer determination or standardization of a volumetric solution used for titration is one of the most important preconditions for reliable and transparent titration results (Straub-Jubb, 2018). Accurate and reliable titration results are only achievable when the exact concentration of the volumetric solution is know. The nominal concentration of a volumetric solution used as a titrant in the titration process is known. The concentration could differ from the real concentration because of a variety of influences. The necessity to determine the real concentration with a titrimetric standard is import in order to obtain correct titration results (Straub-Jubb, 2018). The titer is defined as the quotient of the nominal concentration of a volumetric solution and the actual concentration. The calculated

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factor is then used as the correction factor to the titrant. The measured value of the titer is multiplied with the nominal concentration (Straub-Jubb, 2018).

Materials and methods

Materials

Fatty alcohols and fatty acids are excipients that are abundantly used in various pharmaceutical formulations. Two raw materials will be used: Oleyl alcohol and Miglyol 812. Oleyl alcohol or cis-9-octadecen-1-ol, is an unsaturated fatty alcohol with the molecular formula $C_{18}H_{36}O$. Primarily used in cosmetic and pharmaceutical preparations where advantage is taken of their light color, low odor and fluidity. They are used as the free alcohol in creams and lotions in which they function as emollients and emulsion stabilizers. The oleyl alcohol imparts a smooth, silky feel to the skin (Egan, Earl and Ackerman, 1984). Miglyol 812 is medium-chain triglycerides extracted from endosperms of palm oil and or coconut plants. It consists of a mixture of triglycerides of saturated fatty acids, mainly caprylic acid and capric acid. Miglyol 812 is approved for use in a variety of pharmaceutical formulations including oral, parenteral, rectal and topical products. It is available as a colourless oily liquid that is practically odourless and tasteless (Miglyol 812, Azelis).

Method

The method is from a European pharmacopoeia for which the titration of a potentiometer has been adapted. Previously it was worked as a volumetric titration using burette, conical flask, titrant and sample. In order to replace this method, the burette is replaced with a potentiometer. Analytical procedure: Dissolve 10.00 g of the substance or the quantity prescribed, (g), in 50 mL of a mixture of equal volumes of ethanol (96 per cent) and light petroleum. Titrate with 0.1 M potassium hydroxide (KOH) or 0.1 M sodium hydroxide (NaOH), determining the end-point potentiometrically.
Equation = 5.611(factor) x (end point volume x titer) / weight of sample (Ph.Eur. 2.5.1, current ed.).

Results and discussion

The acid number was determined on both raw materials (Oleyl alcohol and Miglyol 812) with automatic potentiometric titration and volumetric manual titration on 6 consecutive samples. The titration is performed automatically with potentiometer and volumetric-manually in order to confirm the uniformity of the results of the six samples. The difference is that the potentiometer allows the accuracy of the results up to four decimals, as opposed to the volumetric titration up to two decimals, which amazes us with twice the precision and accuracy. Conducted analyzes to determine the acid value of Oleyl alcohol and Miglyol 812 potentiometrically and volumetrically have an overall RSD of 0.15% for Oleyl alcohol and overall RSD of 0.13% for Miglyol 812. The potentiometric determination results for the six samples are identical to the third decimal place.

Conclusion

With the conducted analyzes we prove that this method has the possibility to be adapted, and in the future to be determined using a potentiometer. Automatic determination of acid value gives us a great advantage. That is, with this method we do not use an indicator, which saves resources. It gives us twice as much accuracy and precision. And final this method avoids confusion about the end point volume of the visual difference of pink color by which is the final volume required for the calculation of the acid value is determined.

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