Potentiometric Determination of the Acid Number of Oils and Fats

In the context of process and quality control, the demand for pH measurements and titrations in non-aqueous media is increasing – primarily in the foodstuff and pharmaceutical sector. In accordance with DIN 19260 the pH value can be defined in aqueous media only, a pH measurement is not possible in non-aqueous solutions from the outset or can only be conducted at substantial equipment and scientific cost.

Instead, the acid number can be used for the characterisation of free, organic acids in fats, fatty oils, solvents and tensides [2]. The acid number is one of the lipid values and includes all acidic functions that can be neutralised by potassium hydroxide solution. It specifies the KOH mass in mg that is required for the neutralisation of the acids contained in 1g of the sample to be examined (DIN EN ISO 2114) and can be determined by titration.

Depending on the sample substance, the acid number is used either for identity determination or as a test of purity. For example, fresh waxes that contain free fatty acids permit the determination of the identity, like a ‘fingerprint’ as it were.

On the other hand, the acid number in fresh fats is very low since hardly any free fatty acids arise. If the fats are stored in light and air, the acid number rises substantially with advancing hydrolysis. The chains break up on decay. In this way, the acid number provides information on the age and consistency of fats and oils.

Due to the absence of non-aqueous buffer solutions and the changed ion product in non-aqueous solutions, the voltage level supplied from pH electrodes cannot be converted into a pH value. This means that calibration of the electrode in pH values is not possible [1].

However, because the voltage of the electrode via the real Nernst factor is directly proportional to the pH value of the solution, the mV value can be used in the described procedure without loss of information instead of the pH value.

The measurement in non-aqueous media becomes more difficult with agitated and unstable measured values due to the substantially lower conductivity of the solutions compared with water. For this reason, the internal electrolyte of the electrode must be adapted to the measuring medium. The internal electrolyte preferably consists of a 3M ethanol lithium chloride solution.

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In order to ensure a short response time of the electrode, it must be conditioned for approximately half an hour in the solvent mixture consisting of equal parts of 5M ethanol lithium chloride solution and diethyl ether before the measurement.

The 5M solution is contingent on the solubility. For the measurement, 2-3g of the oil or fat sample must be homogeneously dissolved in a mixture of equal parts of 5M ethanol lithium chloride solution and diethyl ether (approximately 100ml each). It is essential to know the precise initial weight MP in order to calculate the acid value.

The titration is carried out with an ethanol 0.1 M potassium hydroxide solution and results in the electrode voltage versus supplied quantity of KOH [U (V)] function.

The end point is the turning point of the curve with the steepest gradient.

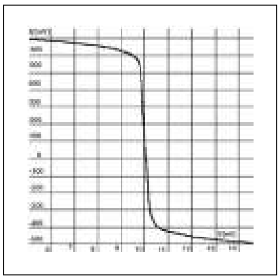

Figure 1. Determination of the end point (turning point).

Due to the ‘smeared’ curve shapes, graphic evaluation procedures are rarely used whereas, in contrast, the computational procedure always leads reliably to determination of the turning point. The well-known turning point condition (zero setting of the 2nd derivative) is required:

$$\frac{d^2U\,(V)}{dV^2} = 0$$

Since the formula of the titration function is unknown but a value table with constant, sufficiently small intervals is available, the differential quotients can be replaced by the potential differences Δ_1.

Value table (excerpt)

V[ml]	U[mV]	$\|\Delta_1\|$	Δ_2
9.50	+573		153
		173	
(9.75)=V_1	+400		$(127)_1$
		(300)*)	
(10.00)=V_2	+100		$-(30)_2$
		270	
10.25	-170		-122
		148	

$|\Delta_1|$ is the positive difference between two adjacent potentials U; Δ_2 is the difference between two adjacent Δ_1 values ($\Delta_{1,\,n+1} - \Delta_{1,\,n}$)

$|\Delta_1|$ = max (*) describes the volume step with the greatest change in potential at the turning point and which is framed by V_1 and V_2. The consumption of potassium hydroxide (V_E) up to the end point (turning point) is interpolated with the aid of a second difference Δ_2 at the V_1 and V_2 points.

$$\frac{f''(V_1)}{f''(V_1) + f''(V_2)} = \frac{\Delta_2\,(V_1)}{\Delta_2\,(V_1) + \Delta_2\,(V_2)} \quad \text{because} \quad f''(V_E) = \Delta_2\,(V_E) = 0$$

The titration curve U(V) is a 3rd order curve in the vicinity of the turning point. $f'' = U''(V)$ therefore represents a straight line. Hence, V_E can be calculated by forming the ratio of the $|\Delta_2(V_1)|$ and $|\Delta_2(V_2)|$ distances.

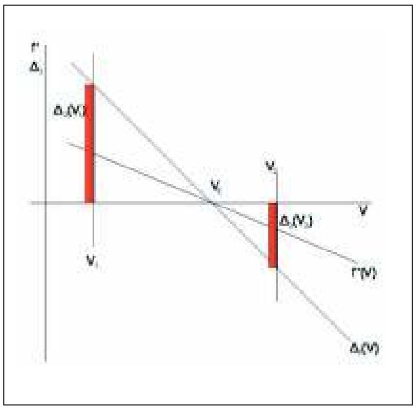

Figure 2. Geometric interpolation of the KOH consumption.

$$V_E = V_1 + \frac{|\Delta_2\,(V_1)|}{|\Delta_2\,(V_1)| + |\Delta_2\,(V_2)|} \times (V_2 - V_1)$$

The acid number is calculated according to the following formula:

$$SZ = \frac{5{,}610 \times V_E}{M_P}$$

where V_E = consumption of 0.1 M KOH solution up to the end point in [ml] (5.610mg of KOH are contained in 1ml of 0.1 M KOH solution) and M_P = initial weight of the sample substance in [g].

REFERENCES

[1] Sound, I und Becker H.: ‘Grenzen der pH-Messung in nichtwässrigen Systemen’ – Laborpraxis November 2007

[2] www.pharm.uni-duesseldorf.de/studium/semester_6/forms/seminare_1.pdf

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