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DETERMINATION OF TOTAL FREE ACID IN FORMALDEHYDE BY COULOMETRIC CATALYTIC THERMOMETRIC TITRATION

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Coulometric catalytic thermometric titration of the total free acid (HCOOH) in formaldehyde of various manufacturers was successfully performed. The indicator reaction was the exothermic polymerization of formaldehyde in the presence of ethanol, catalyzed by strong base. In the titrations, a cathodically polarized platinum generator electrode was employed. The content of free acid in various formaldehyde samples ranged between 0.018 and 0.044 %, and was determined with a standard deviation less than 1.5%. Good agreement was obtained with the results of coulometric photometric and volumetric titrations.

Apart from methanol, which serves for stabilization, aqueous solutions of formaldehyde contain minor amounts of formic acid. The latter must often be determined as accurately and simply as possible. As concerns the titrimetric methods, this determination has previously been performed using standard solutions of strong bases with visual [1–3,5], potentiometric [1,4,5] and catalytic thermometric [5] end-point determination.

In catalytic thermometric titrimetry the methods are based on titration of systems in which the first excess of the titrating reagent catalyzes, directly or indirectly, a side („indicator") reaction, the heat effect of this being the basis for the titration end-point determination. The catalytic action of strong bases in aqueous solutions of formaldehyde leads to polymerization, which results in the formation of a mixture of oxyaldehyde and oxyketon [6]. In the presence of alcohol (e.g. methanol, ethanol, etc.) these reactions are accompanied by an exothermic effect, which we have successfully applied for end-point detection in the volumetric titration of acids [5]. A small excess of the titrant after neutralization of the free acid causes a large and easily measurable temperature change, so that the developed method has proved to be very sensitive.

In this paper we describe a coulometric method for estimation of the total free acid in aqueous formaldehyde, using catalytic thermometric end-point determination.

Experimental

Chemicals and solutions

The total content of free acids (expressed as HCOOH) was tested in aqueous formaldehyde (35%) of various manufacturers: HINS-Novi Sad, Kemika-Zagreb, Merck-Darmstadt, Alkaloid-Skopje.

A 0.1 mol.dm^{-3} sodium perchlorate solution in ethanol served as the supporting electrolyte.

In photometric determinations 0.2% thymol blue in ethanol was used as the indicator. The titrant was 1.10^{-2} mol.dm^{-3} potassium hydroxide in ethanol. It was prepared in the usual way and standardized by titration against benzoic acid with potentiometric end-point determination.

95% ethanol was used as the solvent, without prior purification.

Apparatus

Apparatus for coulometric catalytic thermometric titrations, consisting of a generator and thermometric circuit, was set up in the usual way [7,8].

A cathodically polarized platinum generator electrode was used in the titrations, with a generator current intensity of 2.50–2.70 mA.

The temperature of the solution investigated by catalytic thermometric titration was measured with a Kőbányai Porcelángyár 4TH4 thermistor, which was connected to the recorder through a Wheatston bridge.

The course of coulometric titration was followed by photometry for comparison.

In volumetric determinations continuous addition of the titrating reagent was achieved with a 2.5 cm^3 Radiometer ABU 12 piston burett. The rate of addition of the reagent was 0.143 cm^3.min^{-1}. In potentiometric titrations a glass electrode was used as the indicator electrode, coupled to a saturated calomel electrode. The potential changes were followed with a Radiometer phM 26 pH-meter, which was connected to a Servogor 2S RE 571 (Goerz) recorder through a suitable RC circuit.

Procedure

The total content of free acid (HCOOH) in formaldehyde was determined by catalytic thermometric titration in the following way: 3–5 g formaldehyde was measured into the cathodic compartment of an H-type coulometric cell and 4.5 cm^3 supporting electrolyte solution was added. The latter was also simultaneously poured into the anodic compartment in order to keep the same level of solution in both compartments. The thermistor was immersed into the investigated formaldehyde solution, and both cathodic and anodic compartments were closed with rubber stoppers. The titration was initiated, with the simultaneous connection of the generator circuit and starting of the pen of the recorder.

Blank titrations were performed on identical amounts of formaldehyde to which various volumes (4.50 and 9.00 cm^3) of the supporting electrolyte had been added. The difference of these results was the blank value by which the results of titrations were corrected.

In photometric titrations the procedure was identical as above. Since the measurements had to be performed in a larger coulometric titration cell, it was necessary to add a larger volume of the supporting electrolyte (13.0 cm^3) and 4 drops of 0.2%

ethanolic solution of thymol blue indicator. (The colour change was from yellow to bluish-green.)

The procedure in columetric determinations was different only in the mode of addition of the titration reagent.

Discussion

Typical titration curves of the total free acid in formaldehyde are given in Fig. 1.

The end-point was determined from the intersection of extrapolated straight segments of the curve before and after the equivalence point.

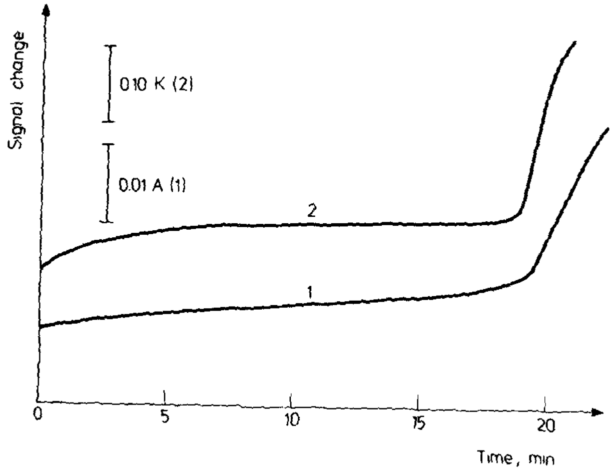

Figure 1 Coulometric titration curves of free acid (HCOOH) in 3.2 g formaldehyde (Alkaloid-Skopje) with photometric (1) and catalytic thermometric (2) end-point determination. Supporting electrolyte: sodium perchlorate, 0.1 mol dm^{-3}, generator current intensity 2.70 mA

The results of titrations were compared with those of volumetric titrations with derivative potentiometric or catalytic thermometric end-point determination. Some of the results are given in Table 1. The coulometric titration data are in agreement with those of volumetric titrations. Hence, this method appears to be of practical interest since it can be successfully applied for the rapid determination of the total free acid (HCOOH) in aqueous formaldehyde.

Table 1 Results of coulometric and volumetric titrations of free acid (HCOOH) in formaldehyde of various manufacturers (averages of 6 runs)

Origin of formaldehyde	Coulometric titration				Volumetric titration			
	Catalytic thermometric		Photometric		Catalytic thermometric		Potentiometric	
	a	s	a	s	a	s	a	s
HINS-Novi Sad	0.018	0.2	0.018	0.1	0.018	0.2	0.017	0.7
Kemika-Zagreb	0.019	1.4	0.019	1.4	0.019	0.7	0.019	0.2
Merck-Darmstadt	0.036	1.4	0.035	0.9	0.035	0.3	0.034	0.7
Alkaloid-Skopje	0.044	1.5	0.043	0.2	0.043	0.3	0.042	0.7

a – found, %
s – standard deviation, %

*

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Zusammenfassung — Die coulometrische katalytisch-thermometrische Titration der Summe der freien Säuren (HCOOH) in Formaldehyd verschiedener Produzenten wurde erfolgreich ausgeführt. Als Indikatorreaktion wurde die exotherme Polymerisation des Formaldehyds in Gegenwart von Äthanol herangezogen, die durch starke Basen katalysiert wird. Zur Titration wurde die kathodisch polarisierte Platingeneratorelektrode verwendet. Der Gehalt an freien Säuren der verschiedenen Formaldehydproben lag zwischen 0.018 und 0.044% und konnte mit einer Standardabweichung von weniger als 1.5 % bestimmt werden. Es ergab sich eine gute Übereinstimmung mit den Ergebnissen von coulometrischen, photometrischen und volumetrischen Titrationen.

Резюме — Успешно проведено кулонометрическое каталитическое термометрическое титрование общего количества свободных кислот в формальдегиде, выпускаемого различными заводами. Индикаторно реакцией была экзотермическая реакция полимеризации формальдегида в присутствии этанола и катализируемая сильными основаниями. При титровании был *исполбзован катодно-поляризационный платиновый электрод*. Содержание свободных кислот в различных образцах формальдегида изменялосб между 0.018 и 0.044%, что было определено со стандартным отклонением меньше чем 1.5%. Данные хорошо согласуются с результаттами кулонометрического фотометрического и объёмного титрований.