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A Thermogravimetric Study of the Stability under Heat of Iron–Protein Complexes

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Iron–protein complexes were investigated by methods of differential gravimetric and differential thermal analyses. Studying the thermal stability has shown that, under heating, these complexes undergo two basic stages of thermal dissociation: dehydration (180–240°) and decomposition of the dehydrated complex (300–700°). Differences in heat dissociation of metal–protein complexes show the varying stabilities of their chemical bonds. It was also found that an additional introduction of ferric ion (Fe^{3+}) decreases the stability of iron–protein complexes.

One of the prime indicators of beer quality is its colloid-protein stability (Badgley, 1972; Stage, 1972; Steiner, 1972; Schildbach, 1971; Narziss and Roettger, 1973). This depends on the amount of metal–protein complexes in aqueous ethanol medium. Information on the concentration of metal-protein complexes in ethanol media is scarce in the scientific literature (Clapperton, 1971; Stone, 1972; Lundin, 1963; Djurtoft, 1962). In previous works (Fertman and Gorinstein, 1970; Gorinstein, 1973a, b), it was proven that the strength of the bonds between microelements and proteins is measured by the ratio of their quantity in protein fractions to their total content in beer. The data have shown that the most common complexing agents are elements of the eighth group (iron) of the Periodic Table of the Elements (Bagger, 1969; Davies *et al.*, 1969; Gorinstein, 1973a).

In order to study the differences in composition between complexes with and without Fe^{3+}, we added Fe^{3+} at a concentration of 3.5×10^{-3} mg/l. The deposition limit of beer (*i.e.*, its stability) sharply decreases as the Fe^{3+} concentration increases (Gorinstein, 1973b). By using the above concentration, a sediment was formed in the beer.

In this study, we have undertaken to isolate the iron-protein complexes, establish their change in composition by heat dissociation, and study their thermal stabilities.

MATERIALS AND METHODS

The investigation was carried out on "Zhiguli" nonfiltered beer, produced at Lvov Brewery Firm "Kolos," from 60% light malt and 40% nonmalted adjuncts. Standards of comparison for beer were the brews clarified by cotton filtering masses "Kineshma" (control) and "Evlakh" (test). (Kineshma and Evlakh are the Russian names of samples of cotton fibers. The Kineshma mass is of 34 nephelos units, and the Evlakh of 55 nephelos units. The two are distinguished by their filtering abilities.)

The stability of iron-protein complexes was determined thermochemically (Paulik *et al.*, 1958; Belcher *et al.*, 1960; Keattch, 1967; Gorinstein, 1974). Proteins were concentrated by tannin–caffeine and ammonium sulfate (for details see Fertman and Gorinstein, 1968). The sediment was dried at 30°. Their thermal stability was studied by the thermogravimetric method using the Paulik–Paulik–Erdey derivatograph (Paulik *et al.*, 1958). Four curves were recorded simultaneously on the derivatograph and are presented in Figures 1–4. Curve 1 on all the figures in positions A and C is the curve of differential thermogravimetric analysis, DTG; curve 2 is the curve of differential thermal analysis, DTA; curve 3 is the curve of temperature, *T*; curve 4 on positions B and D is the curve of integral thermogravimetric analysis, TG. Points a–h are the sites of the endothermic effects of substance weight loss at varying temperatures. The investigated substance and the standard—aluminum oxide repeatedly heated—were heated in a platinum crucible. The conditions of the experiment are as follows: weight of substance, 100 mg; thermopair, Pt-Pt/RH; resistance of electric circuit, DTA, 0.1; DTG, 0.1 megohm; rate of heating, 10°/min; range of error of temperature, ±5°. Twelve samples of iron–protein complexes in beer were investigated.

RESULTS AND DISCUSSION

Investigation of iron–protein complexes by the thermogravimetric method has shown that in the temperature interval of 180–240°, one or two endothermic effects of dehydration take place on the DTG and TG curves of all the samples of beer (see Figures 1–3). The nature of the complex is dependent on the radius and the electrical charge of the heavy metals (Fe, Cu, etc.), and dependent on them, in turn, is the temperature of hydration (Kapitonova *et al.*, 1971; Caldin, 1972; Krestov and Kurakina, 1973).

The first endo effect exists in each of the derivatograms presented in Figures 1–3. In the test beer, however, a higher temperature is found than in the other samples. A quantitative interpretation of the different thermoanalysis curves is presented in Table I.

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