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# The Quality and Authenticity Markers of Tomato Ketchup

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## Abstract

The selected quality and authenticity markers of tomato ketchup were determined in 3 sets of ketchup. The qualitative criteria (colour, pH, hydroxymethylfurfural) were evaluated in commercial samples of ketchup. Authentic markers (formol number, citric and malic acid, pyrrolid-5-one-2-carboxylic acid, and minerals $K^+$, $Mg^{2+}$, $Ca^{2+}$) were determined in model prepared samples and real samples with known natural tomato soluble solids content of the same producer.

**Keywords:** authentication, quality, tomato ketchup

## Introduction

World-wide, tomatoes (*Lycopersicon esculentum*) constitute an important agriculture crop and an integral part of the human diet. Although tomatoes are commonly consumed fresh, over 80% of the tomato consumption comes from processed products (Rao et al. 1998, Thakur et al. 1996). Ketchup is the product that is generally made from tomato paste after diluting on 15% of the soluble solids. It is flavoured with sugar, salt, vinegar, spices, red pepper extract or other ingredients, such as onion, garlic, extracts of spiced herbs and the like (Drdák 1989, Intelmann et al. 2005). Commercial ketchup can have an extremely variable composition; nearly all manufacturers have a formula of their own which differs in some respects from those of other manufacturers. These differences are mainly in the quantity, number and amount of spices or other flavouring agents used. Thus, it is difficult to establish the analytical parameters on which quality depends (Sharoba et al. 2005). Slovak food law (Decree Ministry of Agriculture and Ministry of Health Slovak Republic No. 2089/2005-100 (2006)) specifies the minimum tomato content in ketchup being 7% or 10% natural tomato

soluble solids (NTSS) in total soluble solid content, which is less or more than 30% (Decree Ministry of Agriculture and Ministry of Health of Slovak Republic No. 2089/2005-100 (2006). The minimum tomato content is defined well and explicitly but there exists no legal base at present that would lead to the product quality claims. Moreover, the manufacturers are under the pressure of big distribution chains to produce cheaper products with lower tomato content. The next factor affecting the present situation is the fact that consumers still prefer rather low prices of the product than its quality.

Evaluation of food authenticity is often based on the analyses of selected chemical markers, usually the components of raw materials which are used (and declared) for the product production. The reliability of the authenticity evaluation depends on various factors especially on the variability of raw materials. In the case of plant products (fruits and vegetables) it is especially variety, agricultural conditions, season, degree of maturity, physiological stage, microbial spoilage, etc. The followed markers, the content of those in raw materials can also undergo to various subsequent change due to the post-harvest treatment, storage, production of food products and their storage and distribution (Soukupová et al. 2004).

The most important chemical markers suitable for tomato ketchup authenticity including lycopene, β-carotene, glutamic acid, pyrrolid-5-one-2-carboxylic acid (PCA), citric acid, malic acid, $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ ions and formol number. Some of these markers can be changed during production and distribution. (Soukupová et al. 2004, Otteneder 1986).
As for all products, marketing of tomato products is influenced by their quality. One of these, colour has a strong influence on the buying behavior of the consumer. In the case of tomatoes and tomato products, colour serves as a measure of total quality. Colour in the tomato is due to the presence of carotenoids. Lycopene is the major carotenoid, comprising about 83% of the total pigment present with β-carotene accounting for about 3 to 7% of the total. The quantity of carotenoids in tomato products is dependent on the tomato variety, growing conditions, time and temperature of processing (Hayes et al. 1998, Thakur et al. 1996).

The technological processes used in food production fundamentally impact on the nutritional and biological value of food and, in most cases, also on its sensory quality (Vorlová et al. 2006). Hydroxymethylfurfural (HMF) is a recognized indicator of quality deterioration, as a result of excessive heating or storage in a wide range of foods containing carbohydrates (Rada-Mendoza et al. 2002). HMF is spontaneously formed by the Maillard

reaction (the non-enzymatic browning) or the acid-catalyzed dehydration of hexoses. HMF is practically absent in fresh and untreated foods, but its concentration tends to rise as a result of heating processes or long-term storage (Spano et al. 2006).

The objective of this study was to evaluate of some analytical parameters that are important from quality and authenticity aspects. The results were compared with requirements of Decree of Slovak Republic, Commission Regulation (EEC) and International Federation of Fruit Producers (IFFP) (Decree Ministry of Agriculture and Ministry of Health Slovak Republic No. 2089/2005-100 (2006), Commision Regulation (EEC) No 1764/89 1986, Apaiah and Barringer 2001).

## Materials and Methods

### *Samples of tomato ketchup*

First set consisting of 11 ketchup samples of one Slovak producer with known NTSS of approximately 7.0%; second set – 4 ketchup model samples prepared by the same Slovak producer with defined NTSS (6.0%, 6.5%, 7.5% and 8.0%) and in the last set were 10 ketchup samples (AK-JK) purchased in local Slovak supermarkets. These last samples were come from Slovak Republic, Czech Republic and Poland.

### *Methods of basic physical-chemical parameters*

The soluble solids, pH and formol number were ranked among the basic physical-chemical parameters. The soluble solids was determined with Abbe refractometer AR 2 (KRÜSS OPTRONIC GmbH, Germany) at 20 °C; pH value was measured in pH meter InoLab Level 2 (WTW, Germany) (Commision Regulation (EEC) No 1764/89 1986); formol number were determined by the titration (STN EN 1133 2000).

### *UV-HPLC determination of HMF*

HMF was determined by the following chromatographic system: SpectraSystem P2000 (Watrex, Germany) equipped with a 20 µl sample loop and an UV detector 759A Absorbance Detector (Applied Biosystems, USA). There was used Reprosil 100 $C_{18}$ column, 250 × 4 mm, 5 µm (Watrex, Germany) Separations were carried out isocratically at room temperature using a mixture of acetonitrile-water (5:95, v/v) at flow-rate of 1 $cm^3.min^{-1}$ as the mobile phase,

detection in wavelength at 284 nm. HMF was measured according Ferrer et al. (2002) with some modifications.

15 g of sample was mixed with 5 ml of 0.15 mol. $dm^{-3}$ oxalic acid and 3 $cm^3$ of 40% (w/v) TCA. The mixture was stirred by magnetic stirring plate TC 2 (IKA®-WORKS, Inc., Wilmington, USA) thoroughly for 5 min. It was then centrifuged by the centrifuge MLW K24 (MLW Zentrifugenbau, Engelsdorf, GDR) at 6000 rpm for 15 min. The supernatant was collected and 10 ml of 4% (w/v) TCA was added to the solid residue, mixed thoroughly for 10 min and centrifuged at 6000 rpm for 15 min again. The solid phase was discarded, and the two supernatants were combined. The volume was then measured, and the mixture was filtered through a 0.20 μm filter.

***Colour measurement***

Samples were poured into a clear glass Petri dish and colour parameters (*a** and *b**) were determined using a Chroma Meter Minolta CM-2600d spectrophotometer with software Spectra Magic Ver. 3.3 (Minolta 2001, Japan). The white standard was a piece of tile of known reflectance; the light source $D_{65}$ and the standard observer angle 10° were used (Pipek et al. 2005).

***ITP analysis of organic acids***

Malic, citric acids and PCA acids were determined using an isotachophoretic analyser ZKI 01 (Villa Labeco, Spišská Nová Ves, Slovakia) with conductivity detector and two-line recorder TZ 4200 (Laboratorní přístroje, Praha, Czech Republic). The samples were injected using 30 μl fixed volume.

For citric acid and PCA identification and determination, the electrolytic system of the following composition was applied: leading electrolyte: 10 mmol.$dm^{-3}$ HCl, 0.1% methylhydroxyethyl cellulose (MHEC), aminocaproic acid, pH 4.25; terminating electrolyte: 5 mmol.$dm^{-3}$ caproic acid. The current in the pre-separation column was 250 μA (Kohajdová and Karovičová 2004).

For malic acid analysis electrolytic system consisted of: leading electrolyte: 6 mmol.$dm^{-3}$ L-histidine monohydrochloride, 0.1% MHEC, 6 mmol.$dm^{-3}$ histidine + 2 mmol.$dm^{-3}$ $CaCl_2$, pH 6; terminating electrolyte: 10 mmol.$dm^{-3}$ citric acid. The current in the pre-separation column was 200 μA (Karovičová et al. 2003).

***FAAS determination of minerals***

The minerals were determinate using an atomic absorption spectrometer Perkin Elmer 1100 with flame atomizator (Norwalk, USA). The setting instrumental parameters for individual analytes are shown in Tab. 1.To the 6.00 g of tomato ketchup sample, 10 $cm^3$ of concentrated $HNO_3$ was added and mixed. The mixture was placed in a warm sand bath (temperature approximately 250 °C) and evaporated until the mixture was 1 $cm^3$. After dropping temperature, 3 $cm^3$ of concentrated $HClO_4$ was added and the mixture was heated again. When intensive white smoke appeared, the mixture was taken from sand bath. After smoking, 0.6 $cm^3$ of concentrated $H_2O_2$ was added and the sample was quantitatively poured into 50 $cm^3$ of volumetric flask.

Table 1 The instrumental parameters for determination K, Mg and Ca minerals in ketchup samples using FAAS

| The instrumental parameters | K | Mg[1] | Ca[1] |
|---|---|---|---|
| Wavelength [nm] | 766.5 | 285.2 | 422.7 |
| Supply current of HCL lamp [mA] | 12 | 6 | 10 |
| Gap [nm] | 0.7 | 0.7 | 0.7 |
| Air flow [$dm^3.min^{-1}$] | 2.5 | 2.5 | 3.5 |
| Acetylene flow [$dm^3.min^{-1}$] | 8.0 | 8.0 | 8.0 |

[1] Mg and Ca were measured with addition of elimination solution containing 1$g.dm^{-3}$ La and 5 $g.dm^{-3}$ of 8-hydroxychinoline

## Results and Discussion

In the first part of our work the selected qualitative parameters were determined. They are shown in Tab. 2. The soluble solids content is important preserving factor. The refraction of tomato is used for determination of maturity and suitability for tomato paste production because it affected spending of tomato at concentration on various concentrated tomato paste. As shown in Tab. 2, the soluble solids ranged for ketchup samples from 14.6% (FK) to 32.7% (EK). All samples of ketchup conformed to the standard of Decree of Slovak Republic because that defined only minimum NTSS.

Among the parameters analyzed for the assessment of tomato quality, pH is very important because acidity influences the thermal processing conditions required for producing safe products. Although the pH of mature tomatoes may exceed 4.6, tomato products are generally classified as acid foods (pH < 4.5), which require moderate conditions of processing to control microbial spoilage and enzyme inactivation (Garcia and Barrett 2006, Hayes et al. 1998). Tomato products shall have a pH not exceeding 4.5 (Commision Regulation (EEC) No 1764/89 1986). The pH values were ranged between 3.6 and 4.3, so all samples fulfilled this requirement.

Table 2 The selected qualitative parameters in tomato ketchup samples

| **Sample** | **Soluble solids [%]** | **pH** | **HMF [mg.kg$^{-1}$]** | ***a*/b**** |
|---|---|---|---|---|
| 1 K | 25.0 | 4.2 | nd | 2.1 |
| 2 K | 24.0 | 4.2 | nd | 2.0 |
| 3 K | 25.0 | 4.2 | nd | 2.0 |
| 4 K | 25.0 | 4.3 | nd | 2.0 |
| 5 K | 25.1 | 4.3 | nd | 1.9 |
| 6 K | 24.5 | 4.2 | nd | 2.0 |
| 7 K | 25.1 | 4.3 | nd | 2.0 |
| 8 K | 25.2 | 4.1 | nd | 2.0 |
| 9 K | 24.5 | 4.2 | nd | 2.1 |
| 10 K | 24.6 | 4.2 | nd | 2.1 |
| 11 K | 24.6 | 4.2 | nd | 2.0 |
| K 6,0 | 25.0 | 4.3 | — | — |
| K 6,5 | 25.5 | 4.3 | — | — |
| K 7,5 | 25.1 | 4.3 | — | — |
| K 8,0 | 25.5 | 4.3 | — | — |
| AK | 25.9 | 4.1 | 22,44 | 1.6 |
| BK | 25.5 | 4.3 | 16,53 | 2.0 |
| CK | 27.8 | 3.9 | 2,98 | 2.0 |
| DK | 23.4 | 4.0 | 18,24 | 1.7 |
| EK | 32.7 | 3.9 | 2,95 | 1.6 |
| FK | 14.6 | 3.6 | 7,83 | 1.6 |
| GK | 28.2 | 4.1 | 28,40 | 2.2 |
| HK | 27.3 | 3.9 | 7,90 | 1.8 |
| IK | 28.2 | 3.8 | 4,33 | 1.8 |
| JK | 26.5 | 4.1 | nd | 2.1 |

HMF is a recognised indicator of reduced quality in numerous foods that contain carbohydrate (Vorlová et al. 2006). According to the International Federation of Fruit Producers, a HMF content greater than 25 mg.kg$^{-1}$ for concentrates is excessive. Larger

concentrations indicate overheating of tomato products (Apaiah and Barringer 2001). From the Tab. 1 we can see the content of HMF in the interval from 2.95 $mg.kg^{-1}$ (EK) to 28.40 $mg.kg^{-1}$ (GK) for ketchup samples. HMF was not detected in the ketchup JK.

Colour may serve as an indicator of freshness because extensive processing often goes along with the deterioration of the typical colour. In order to maintain the native tomato colour in tomato ketchup, processing must be kept at minimum, and storage at high temperatures, exposure to sunlight, and the storage in retail containers permeable to oxygen must be avoided (Intelmann et al. 2005). The *a*/b** ratio is used as a quality specification for tomato products. Values of 1.9 and above are indicative of an excellent colour, while a value below 1.8 is considered unacceptable (Barreiro et al. 1997). The *a*/b** ratio below 1.8 was determined in 4 ketchup samples AK, DK, EK and FK.

In the Tab. 3 are shown authentic markers analyzed in first and second series of tomato ketchup samples. From the research obtained by Soukupová et al. (2004) it is concluded that the concentration of cations ($K^+$, $Mg^{2+}$, $Ca^{2+}$), malic and citric acids content and formol number are relatively stable parameters.

Table 3 The authentic markers of tomato ketchup samples

| **Sample** | **Formol number [$cm^3$ 0,1 M NaOH/100 g]** | **Citric acid [mg/100g]** | **Malic acid [mg/100g]** | **PCA [mg/100g]** | **$K^+$ [mg/100g]** | **$Mg^{2+}$ [mg/100g]** | **$Ca^{2+}$ [mg/100g]** |
|---|---|---|---|---|---|---|---|
| 1 K | 40.7 | 527.6 | 64.9 | 258.3 | 354.9 | 14.6 | 18.5 |
| 2 K | 38.4 | 576.3 | 70.5 | 190.3 | 327.2 | 13.6 | 17.6 |
| 3 K | 43.6 | 559.2 | 67.4 | 143.8 | 367.8 | 14.3 | 18.3 |
| 4 K | 38.7 | 498.4 | 54.0 | 182.7 | 306.1 | 14.7 | 21.8 |
| 5 K | 50.7 | 587.6 | 67.5 | 159.4 | 331.8 | 15.2 | 23.1 |
| 6 K | 45.1 | 643.1 | 72.9 | 237.8 | 287.5 | 15.6 | 20.5 |
| 7 K | 50.5 | 503.5 | 68.2 | 195.8 | 303.4 | 15.7 | 24.3 |
| 8 K | 39.0 | 601.0 | 57.6 | 211.8 | 332.6 | 13.9 | 17.8 |
| 9 K | 44.1 | 708.2 | 56.4 | 157.0 | 372.4 | 15.6 | 18.5 |
| 10 K | 45.6 | 582.3 | 60.3 | 222.2 | 357.6 | 15.0 | 18.1 |
| 11 K | 43.1 | 588.9 | 58.4 | 181.8 | 365.0 | 14.7 | 18.5 |
| K 6.0 | 31.2 | 574.6 | 54.1 | 190.3 | — | — | — |
| K 6.5 | 36.4 | 585.0 | 61.6 | 198.5 | — | — | — |
| K 7.5 | 57.3 | 639.3 | 70.3 | 217.1 | — | — | — |
| K 8.0 | 64.9 | 673.3 | 77.4 | 228.3 | — | — | — |

The determination of the formol number represents a further parameter for the characterisation of the tomato products. It corresponds to the amino acid content and therefore it is one of the authentication markers. Its content was varying from 38.4 to 50.5 $cm^3$ 0.1 M NaOH/100 g in first set of tomato ketchup samples with approximately 7.0% NTSS.

The predominant organic acids of raw tomatoes are citric and malic acids, which can be considered as authentication markers. Their content can be affected by the degree of maturity. Citric acid is also very often used as acidulant to reduce pH value during the tomato paste production. The content of citric acid was varying from 498.4 g to 708.2 mg /100 g and malic acid from 54.0 to 72.9 mg/100 g in first set of ketchup samples.

PCA is formed during the tomato processing from glutamine or glutamic acid. The PCA content in ketchup depends on the concentration of precursors and also on the temperature history during the processing. Heating enhances the rate of formation (Soukupová et al. 2004). Its content in first analyzed set of samples was ranged from 143.8 to 258.3 mg/100 g.

The minerals content was analyzed only in first set of samples. Potassium occurs commonly in many food products, especially in fruits and vegetables. To foods containing a lot of potassium belong tomato products, too. However KCl can be included in the recipe to reduce the NaCl content. Calcium cations could be present in water. The content of single minerals was following: $K^+$ from 287.5 to 372.4 mg/100 g, $Mg^{2+}$ from 13.6 to 15.6 mg/100 g and $Ca^{2+}$ from 17.6 to 24.3 mg/100 g.

As we can see from our study, the authentic markers of commercial ketchup of one Slovak producer with approximately 7.0% NTSS are not correlating reciprocally. On the other side markers of model sample of ketchup are correlating well. There are many factors that influenced the content of individual authentic markers in real tomato ketchup samples. Therefore we propose to establish absolute (min/max) requirements for authentication of tomato ketchup as it is in other food products (for example honey, fruit and vegetable juices). In order to establish limits of these markers, the cooperation with more producers of ketchup is desirable, because of variability of tomato fruits (variety, agricultural conditions, season, degree of maturity, physiological stage, microbial spoilage, etc.) and processing.

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