Preservation and analysis of food samples

REPORT ON TRAINING VISIT

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PREFACE

I, Dipl. Ing. Nafisa Rokai at 25th March 2011 came from Kabul, Afghanistan to Bratislava, Slovakia for a study and scientific research. This program was organized in the form of project works for development the Human Resource Capacity of Engineering Education in Afghanistan. The project was coordinated by the Slovak University of Technology in Bratislava for Kabul Polytechnic University teachers.

I am working at the Kabul Polytechnic University (KPU) at the Chemical Technology Faculty. This Faculty has six departments: Chemical Technology Fundamentals, Technology of Organic Materials, Technology of Inorganic Materials, Food Technology and Metal Processing and Chemistry department. This Faculty was established in 2009 on the base of chemical technology department, which works since 1971. The Food Technology department began working in 2010 and Metal Processing department will be open in the near future. The Chemical Technology department had several laboratories, but they were destroyed during the civil war. Now we don’t have any standard laboratories for our department and we are teaching students without laboratory practices. But we hope, that the KPU senior management will prepare opportunities for laboratory practices as soon as it will be possible to equip the laboratories. This scientific activities report was prepared during my stay from 25th March 2011 to 1st June 2011 at the department of Biotechnology and Food Technology of Slovak Technical University in Bratislava, Slovakia.

This report has two parts: Part 1. Academic and scientific activities
Part 2. Experimental research in laboratories.

The 1st part was carried out by the collection of scientific materials about the topic and experimental methods from internet, available books and articles.

In the 2nd part I done experimental researches about different kinds of methods used by the apple jam and tomato paste preparation. Participating was also international conference organised in High Tatra.

I hope that the following pages will inspire your interest, what I have done during my staying in Slovakia, under guidance of doc. Ing. Jolana Karovičová, PhD. and Ing. Žlatica Kohajdová, PhD.

I would like to thank the Scientific training program organizers for the excellent opportunity of visiting all facilities at the Faculty of Chemical and Food Technology and accommodation and other facilities, allowing me to network and instruction with several professionals from my work field, Professor Juma Haidary - director of the program, leader of the Biotechnology and Food Technology department, Prof. Ing. Stefan Schmidt, PhD and also thanks belongs to a lot the members from this department.

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1. Theoretical section

1.1 Preservation principles and applications

Preservation techniques put into practice the control mechanisms for reducing food deterioration. Often, various methods are combined to ensure safety and preservation action while maintaining maximal quality and stability. For example, fluid milk is preserved through a combination of pasteurization and subsequent refrigeration, aseptic thermal processing is usually combined with aseptic packaging and freezing is usually accompanied by a blanching pretreatment to reduce enzymatic activity (Hui, 1989).

1.1.1 Physical Preservation

Thermal Methods. A number of preservation processes use heat to extend the shelf life of food. High temperature preservation methods performed commercially are controlled processes that include canning, aseptic processing, pasteurization, and blanching. Microorganisms differ in their heat resistance and are classified as psychrotrophs, mesophiles, or thermophiles according to their tolerance to heat. All microorganisms can be destroyed by the application of heat, and each organism has a certain time/temperature relationship associated with it to ensure a given in its population. The most intense heating preservation process would render the food sterile. Sterilization refers to the complete destruction of all microorganisms. Complete sterility is difficult to achieve and often leads to a reduction in the quality attributes of the food since most food components such as proteins or vitamins are also heat sensitive. Commercial sterility has been defined as the destruction of all pathogens and spoilage organisms in a food. Canning, thermal retorting in aluminum cans or flexible pouches, and aseptic processing, thermal before packaging followed by aseptic packaging techniques, target commercial sterility as their goal. Provided the food is maintained in the commercially state after processing, a shelf of 2 years or more can be achieved (Hui, 1989).

Pasteurization is a low order, time- and temperature dependant heating process that is designed to destroy all pathogens present in the food, to reduce the bacterial load in the case of milk and eggs, to reduce the yeast and mold count in the case of wine, and fruit juices, and to extend the shelf life. Pasteurization can be performed before packaging, as in milk, or subsequent to packaging, as in beer. Blanching is another low-order heat process used primarily as a pretreatment step in freezing to destroy enzymes and in canning to wilt and cleanse and expel tissue gas (Hui, 1989).

Low temperature methods include both refrigeration and freezing below 15 °C but above freezing retards growth of microorganisms, retards metabolic activities of animal tissues postslaughter and plant tissues postharvest, retards deteriorative chemical reactions such as oxidation and enzyme-catalyzed reactions, and retards moisture loss. Unlike heating preservation does not destroy microorganisms, only retards their growth. The foods are still perishable and organisms will grow more rapidly once conditions become favorable. The shelf can be extended from less then 1 week for highly perishable such as raw milk or tomatoes to more than 6 months for durable products such as onions or smoked meats. Freezing preservation is achieved through both the low temperatures, which inhibit microbial growth and rates of reactions, and the reduction in water content as a result of ice crystallization. Shelf life of frozen foods can range from 3 months to year or longer, but is still limited by enzymatic activity, oxidation, and dehydration. Commercial food freezing facilities use several methods, including air freezing through sharp (natural convection), blast, or fluidized bed (forced convection) techniques, indirect contact systems such as plate freezers.
or scraped surface freezers, or direct contact freezing systems using low – temperature liquids or cryogens (Hui, 1989).

**Reduction of Water Content.** Microorganisms need favorable moisture conditions within the food, water activity greater than 0,6 to 0,8 for their growth. It is therefore possible to manipulate the water activity of the food to inhibit microbial action. Concentration of liquid food products through thermal evaporation, freeze-concentration, osmotic dehydration, and membrane processes achieves lowered water contents and, provided that water activity has been lowered sufficiently, offers preservation action. Thermal concentration removes water in the form of vapor from the liquid. It is usually performed in multiple-effect film vacuum evaporators for thermal efficiency and product quality. Freeze concentration removes water from liquid foods in the form of ice and is particularly suited to foods such as fruit juices with depressed freezing points due to high sugar concentrations within the food. Osmotic dehydration has been used for fruit in sugar solutions whereby water will migrate from the fruit slice into the sugar solution owing to the high osmotic pressure of the solution. Membrane processes remove water from foods in the form of liquid water. Due to the presence of a semipermeable membrane and the imposition of a pressure gradient. Solvent and low molecular weight solute, depending on the membrane pore size, pass through the membrane in the permeate stream while the higher molecular weight solutes are concentrated in the retentate stream (Hui, 1989).

The nearly complete removal of water through dehydration by solar, cabinet, tunnel, drum, or spray drying methods also offers a form of preservation by reduction of available water for microbial growth. Dehydration occurs under controlled conditions that cause minimal changes in the food properties. The food can then be consumed dried, as in some dried fruits or meats, but is more likely to be rehydrated before consumption, as in dried milk and eggs, instant potato flakes, or instant coffee. The reconstituted product should resemble as closely as possible the quality of the original food. In addition to preservation, the drying of foods decreases the weight and bulk of the original food and adds a measure of convenience to the product. Sun drying has been practiced for centuries and is still employed for the dehydration of grains, seaweeds, raisins, and other foods. Particularly in developing countries, most commercial fruit and vegetable operations employ continuous tunnel or belt dehydration systems that use heated air the drying medium. The majority of liquid foods, such as skim milk, cake and soup mixes, flavors, purees, juices or instant coffee, are dried in spray dryers that atomize the usually preconcentrated liquid product into tiny droplets that dry rapidly in the surrounding environment. Freeze-drying removes water a frozen food through sublimation under vacuum and is particularly suited to thermally sensitive products, such as instant coffee or convenience-type entrees (Hui, 1989).

**Oxygen Control.** Because of the strict oxygen requirements for bacterial growth and the participation of oxygen in a number of chemical reactions, oxygen control can act as a means of food preservation. Controlled and modified atmosphere storage of foods are techniques to maintain gaseous atmospheres with strictly controlled oxygen contents. The controlled atmosphere can be maintained in warehouses for bulk foods, eg, apples, often before further processing or can be maintained at the microatmospheric level within a food package. Food packaging also offers protective barriers to food against the action of contaminating microorganisms, pasts, moisture, oxygen, and light. The packaging necessary to maintain preservation is usually chosen to accompany the particular process. Examples include multilaminate flexible packaging for aseptically processed foods or rigid aluminum cans for retorting (Hui, 1989).

**Radiation.** The use of nuclear energy in the form of γ radiations, short wavelengths emitted by unstable isotopes of cobalt 60, or cesium 137 to inactivate microorganisms has been a developing technology since 1945. The main goal of irradiation is to extend the shelf
life of foods where heat or chemical means are unfeasible owing to the nature or geographic location of the food. Major potential applications of this process include spices, owing to the heat-sensitive volatile flavor components; insect disinfestation of grains and fruit; extended shelf life of fruits, vegetables, fish, shellfish, and meat products; sterilized diets for military, space, and medical uses; and animal feeds and moist pet foods. The irradiation occurs in an enclosed chamber in which the product can be exposed to an even distribution of the penetrating $\gamma$ rays for the necessary time to accomplish microorganism inactivation (Hui, 1989).

1.1.2 Chemical preservation

**Intermediate Moisture Foods.** An intermediate moisture food (IMF) is one that can be eaten as is, without rehydration, and yet is shelf stable without refrigeration or thermal processing. Whereas most foods have water activities in the range 0.9-1.0, IMF foods rely on water activities in the range 0.65-0.85, below that required for the growth of the most tolerant organisms, for their preservation effects. Included in this category of foods are jams and jellies, fruit cakes, pepperoni, sweetened condensed milk, marshmallows, soft cookies, and many others. Sugar and other humectants, water-absorbing compounds such as sorbitol, glycerol, starches, or gelatin, can be used to formulate these foods. Although the technology can produce a range of products with acceptable texture, many of which have been in existence since historical times the flavor profile created by the various humectants has been the major limiting factor in new product development (Hui, 1989).

**pH Control.** Acids can be used to lower the pH of foods to below the tolerable range for microorganisms. Acid can also enhance the lethality of heating processes. *Clostridium botulinum*, the organism of concern in commercial canning processes, will not grow at less than pH 4.5, and thus it is not necessary to thermally process high acid foods ($\text{pH}<4.5$) under the rigid time temperature standards as is the case with low acid foods ($\text{pH}>4.5$). The addition of acid to such foods as soft drinks and the production of acid in some food fermentations are effective controls of microbial growth. However, pH control is normally associated with some other means of preservation as well, as the palatability of many foods and chemical stability of their constituents (eg, proteins) also decreases at low pH levels (Hui, 1989).

**Chemical Addition.** Salt can be added to foods for its contribution to the preservation of the food, eg, butter, fish, or cured meat products such as bacon. The action of salt results from the osmotic pressure created in the aqueous environment surrounding the microbial cell, in an analogous manner to the addition of sugar in intermediate moisture foods or the use of sugar syrups for osmotic dehydration of fruits. Plasmolysis, the partial dehydration of the cell, results and the viability of the microorganism is thus destroyed. Smoke is also a type of chemical preservative that has been used since historical times to preserve foods, especially meat and fish products. The action of smoke results from the formation of small amounts of preservative chemicals and the internal temperatures and dehydration of tissues associated with the hot-smoking process. Cold-smoking at temperatures less than 30°C relies solely on the formation of bactericidal chemicals and is usually associated with other means of preservation such as salting, refrigeration, or packaging. Chemical preservation, such as benzoic acid or sodium benzoate, sorbic acid or potassium sorbate, sodium nitrite or nitrate, and sulfur dioxide, are permitted at low levels in some foods as preservative agents microbial growth. The use of chemical preservatives and other food additives closely regulated by governmental agencies (Hui, 1989).
I. 1. 3 Biological Preservation

Fermentation. Unlike the processes described above food fermentations have as their goal increase in the numbers of microorganisms present in a food. The traditional foods of many countries rely on fermentation processes, and fermentation is an historical but important means of food preservation throughout the world. Fermented foods are preserved through action of a particular organism unique to each given commodity, on a particular substrate within the food product, primarily carbohydrates but also proteins and lipids. The conditions of fermentation favor the growth of the desirable organism, which is often added in the form of a pure culture, and cause the competitive disappearance of undesirable spoilage or pathogenic organisms. The metabolic by-products of the fermentation change conditions such as pH or oxygen content within the food, which also act to inhibit the undesirable organisms. They include lactic and other acids, ethanol and other alcohols, gases such as CO$_2$, and a variety of other compounds at low levels are responsible for the unique flavor characteristics of the particular product. Examples of food fermentations include the production of alcohols by yeasts in wine, cider and beer, and the production of lactic acid by bacteria in fermented milks, sour cream, yogurt, fermented meats, pickles, sauerkraut, and vinegar (Hui, 1989).
1.2. Tomato pasta

The product with highest production volumes among concentrated products is tomato paste which is manufactured in a various range of concentrations, up to 44% refractometric extract. Tomato paste is the product obtained by removal of peel and seeds from tomatoes, followed by concentration of juice by evaporation under vacuum (Singh 2007).

In some cases, in order to prolong production period, it may be advisable or possible to preserve crushed tomatoes with sulphur dioxide as described under semi-processed fruit “pulps“ (Singh 2007).

Technological flow-sheets run according to equipment/installation lay-outs, which are especially designed for this finished product. Manufacturing steps fall into three successive categories (Singh 2007).

1.2.1 Obtaining juice from raw materials

Obtaining juice from raw material – preliminary operations (pre-washing, washing and sorting/control) are carried out in the same conditions as for manufacturing of “drinking“ tomato juice described above. Next operation is removal of seeds from raw tomatoes: tomato crushing and seed separation with a centrifugal separator. Tomato pulp is pre-heated at 55 – 60 °C and then passed to the equipment group for sieving: pulper, refiner and superrefiner with sieves of 1.5 mm, 0.8 mm and 0.4 – 0.5 mm respectively in order to give the smoothest possible consistency to the tomato paste (Singh 2007).

1.2.2 Juice concentration

Juice is concentrated by vacuum evaporation, a technological step which in modern installations runs continuously, tomato paste from the last evaporation step being at the specified concentration (Singh 2007).

In continuous installations with three evaporation steps (evaporating bodies), the juice is submitted in step/body I to pasteurization at 85-90 °C for 15 min and this will determine the microbiological stability of finished product. Vacuum degree corresponding to this temperature is 330 mm Hg (Singh 2007).

In evaporating bodies II and III, temperatures are around 42-46° C and vacuum at 680700 mm Hg. Juice concentration occurs gradually and continuously in the three evaporating bodies (Singh 2007).

The advantages of continuous concentration are as follows:

The taste, colour, flavour, "II shine" and consistency of tomato paste are improved because:

a) The real concentration is performed in evaporating bodies II and III at low temperatures (42-46° C) and
b) The whole concentration process time from the input of juice in body I until the output of paste from body III is of about 1 hour (for paste with 30-35% refractometric extract) (Singh 2007).

Production capacity is raised by about 30% as compared to discontinuous installations with the same evaporation surface; the steam consumption is reduced by 60% because heating of bodies II and II is done with vapours resulting from juice evaporation in
body I (double effect); water and electricity consumptions are also reduced by 30-40 % (Singh 2007).

1. 2. 3 Tomato paste pasteurization

Tomato paste pasteurization assures the microbiological stability of the product. For this purpose, the paste coming out from concentration equipment is passed continuously and in a „forced“ mode through a tubular pasteurizer from which it emerge at a temperature of 90 – 92 °C (Singh 2007).

Usual commercial tomato paste types are at concentrations of 24%, 28% and 32% refractometric extract. Sometimes it is possible to obtain a tomato paste with a concentration of 44% refractometric extract; for this purpose it is necessary to eliminate a part of cellulose from tomatoes, an operation performed in a separating turbine (Singh 2007).

Tomato paste storage and preservation is carried out after packing which is done usually in drums, metallic cans or glass jars; some modern equipment has been developed for packing in aluminium bags. As far as the concentration of tomato paste is concerned it is not possible to reduce water content down to 30% which corresponds to a water activity aw of 0.70 – 0.75 (minimum limit of mould growing), it is necessary to take special measures (e. g pasteurization, cold storage or salt addition) (Singh 2007).

Salt is not a preservative in itself but contributes to the lowering of water activity. In drums, the preservation of tomato paste with minimum 30% refractometric extract is carried out in two ways:
- The hot paste (about 90°C) flows directly from pasteurization equipment into drums that have been previously steamed;
- The paste is cooled down to 30°C through a heat exchanger and is introduced into drums that have been previously steamed (Singh 2007).

For preservation purposes, it is possible to add 3-8% salt. Preservation with 3% salt must be carried out respecting the following criteria:

a) Processing of a healthy raw material;

b) Thorough washing and control;

c) Pasteurization of concentrated paste and use of well prepared drums. Paste in drums has to be stored in cold storage rooms during the hot season (Singh 2007).

Preservation in big metal cans of 5 and 10 kg capacity of tomato paste with a minimum of 30% refractometric extract can be achieved without sterilisation if the following conditions are respected:

a) Sterilisation by steam of cans and covers;

b) Filling of paste at 92-94°C;

c) Airtight sealing/closing of cans;

d) Invert cans and then

e) Air cooling (Singh 2007).

For small packages (tinplate cans of 1/10-1/1 or glass jars of same capacity) it is usual to use pasteurized paste, as hot as possible (92-94°C). The receptacles are first sterilised by steam. After airtight sealing, the receptacles are kept in boiling water for a short time in order to sterilize their inner surface and the paste in contact with inner receptacle surface. In some countries small receptacles are not further sterilised if the manufacturing is carried out in perfect hygienic and sanitary conditions. Packing in small tinned aluminium tubes is carried out with concentrated paste, pasteurized and hot (Singh 2007).
Good quality tomato paste is an homogenous mass, with a high density, without foreign bodies (seeds, peel, etc.), with a red colour, and an agreeable taste and smell, close to those of fresh tomatoes (Singh 2007).

There are usually three types of tomato paste: 36, 30 and 24 which have refractometric extracts of respectively 34-38%, 28-32% and 24-26%. Paste of good quality must have a volatile acidity of maximum 0.15% as lactic acid. An 8% salt addition is accepted (Singh 2007).

References:


1.3 Evaporation

In common with other unit operations that are intended to separate components of foods, evaporation and distillation aim to separate specific components to increase the value of the food. In both types of operation, separation is achieved by exploiting differences in the vapour pressure (volatility) of the components and using heat to remove one or more from the bulk of the food.

Evaporation

Evaporation, or concentration by boiling, is the partial removal of water from liquid foods by boiling off water vapour. It increases the solids content of a food and hence preserves it by a reduction in water activity (Chapter 1). Evaporation is used to pre-concentrate foods (for example fruit juice, milk and coffee) prior to drying, freezing or sterilization and hence to reduce their weight and volume. This saves energy in subsequent operations and reduces storage, transport and distribution costs. There is also greater convenience for the consumer (for example fruit drinks for dilution, concentrated soups, tomato or garlic pastes, sugar) or for the manufacturer (for example liquid pectin, fruit concentrates for use in ice cream or baked goods). Changes to food quality that result from the relatively severe heat treatment are minimised by the design and operation of the equipment. Evaporation is more expensive in energy consumption than other methods of concentration (membrane concentration) and freeze concentration but a higher degree of concentration can be achieved (Table 1).

Theory

During evaporation, sensible heat is transferred from steam to the food, to raise the temperature to its boiling point. Latent heat of vaporisation is then supplied by the steam to form bubbles of vapour, which leave the surface of the boiling liquid. The rate of evaporation is determined by both the rate of heat transfer into the food and the rate of mass transfer of vapour from the food. These processes are represented schematically in Fig. 1.

Table 1 A comparison of energy efficiency and degree of concentration in different methods of concentration

<table>
<thead>
<tr>
<th>Method</th>
<th>Steam equivalent (cost per kilogram of water removed divided by equivalent cost of steam)</th>
<th>Maximum concentration possible (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrafiltration</td>
<td>0.001</td>
<td>28</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>0.028</td>
<td>30</td>
</tr>
<tr>
<td>Freeze concentration</td>
<td>0.090-0.386</td>
<td>40</td>
</tr>
<tr>
<td>Evaporation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triple effect without aroma recovery</td>
<td>0.370</td>
<td>80</td>
</tr>
<tr>
<td>Triple effect with aroma recovery</td>
<td>0.510</td>
<td>80</td>
</tr>
</tbody>
</table>

From Thijsse (1974).
Fig. 13.1 Steady state operation of an evaporator: \( m_f \) (kg s\(^{-1}\)), mass transfer rate of feed liquor; \( m_p \) (kg s\(^{-1}\)), mass transfer rate of product; \( X_f \), solids fraction of feed liquor; \( X_p \), solids fraction of feed product; \( m_v \) (kg s\(^{-1}\)), mass transfer rate of vapour produced; \( m_s \) (kg s\(^{-1}\)), mass transfer rate of steam used; \( \theta_f \) (ºC), initial feed temperature; \( \theta_b \) (ºC), boiling temperature of food; \( \theta_s \) (ºC), temperature of steam.

**Heat and mass balances**

Heat and mass balances are used to calculate the degree of concentration, energy use and processing times in an evaporator. The mass balance states that ‘the mass of feed entering the evaporator equals the mass of product and vapour removed from the evaporator’. For the water component, this is given by:

\[
\frac{m_f}{m_f} (1 - X_f) = \frac{m_p}{m_p} (1 - X_p) + m_v
\]

For solutes, the mass of solids entering the evaporator equals the mass of solids leaving the evaporator:

\[
m_f X_f = m_p X_p
\]

The total mass balance is \( m_f = m_p + m_v \)

Assuming that there are negligible heat losses from the evaporator, the heat balance states that ‘the amount of heat given up by the condensing steam equals the amount of heat used to raise the feed temperature to boiling point and then to boil off the vapour’:

\[
Q = m_f c_p (\theta_b - \theta_f) + m_v \lambda_v
\]

where \( c \) (J kg\(^{-1}\)ºC\(^{-1}\)) = specific heat capacity of feed liquor, \( \lambda_s \) (J kg\(^{-1}\)) = latent heat of condensing steam, \( \lambda_v \) (J kg\(^{-1}\)) = latent heat of vapourisation of water (Table 2). That is:

**Heat supplied by steam = Sensible heat + Latent heat of vaporisation**

The rate of heat transfer across evaporator walls and boundary films is found using equation. \( Q = UA(\theta_s - \theta_b) \). For the majority of an evaporation process, the rate of heat transfer is the controlling factor and the rate of mass transfer only becomes important when the liquor becomes highly concentrated.
Sample problem

A single-effect, vertical short-tube evaporator is to be used to concentrate syrup from 10% solids to 40% solids at a rate of 100 kg h\(^{-1}\). The feed enters at 15\(^\circ\)C and is evaporated under a reduced pressure of 47.4 kPa (at 80\(^\circ\)C). Steam is supplied at 169 kPa (115\(^\circ\)C). Assuming that the boiling point remains constant and that there are no heat losses, calculate the quantity of steam used per hour and the number of tubes required. (Additional data: the specific heat of syrup is constant at 3.960 kJ kg\(^{-1}\)K\(^{-1}\), the specific heat of water is 4.186 kJ kg\(^{-1}\)K\(^{-1}\), the latent heat of vaporisation of the syrup is 2309 kJ kg\(^{-1}\), the overall heat transfer coefficient is 2600Wm\(^{-2}\)K\(^{-1}\) and the latent heat of steam is 2217 kJ kg\(^{-1}\) at 115\(^\circ\)C.)

Solution to Sample problem

To find the quantity of steam used per hour, we find that, from equation

\[
\frac{100}{3600} \times 0.1 = m_{\text{p}} \times 0.4
\]

\[
m_{\text{p}} = 0.0069 \text{ kg s}^{-1}
\]

From equation

\[
\frac{100}{3600} (1 - 0.1) = 0.0069 (1 - 0.4) + m_{\text{v}}
\]

\[
m_{\text{v}} = 0.0209 \text{ kg s}^{-1}
\]

From a mass balance, we find the following table.

<table>
<thead>
<tr>
<th></th>
<th>Solids</th>
<th>Liquid</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>0.00278</td>
<td>0.025</td>
<td>0.0278</td>
</tr>
<tr>
<td>Product</td>
<td>0.00276</td>
<td>0.00414</td>
<td>0.0069</td>
</tr>
<tr>
<td>Vapour</td>
<td></td>
<td></td>
<td>0.0209</td>
</tr>
</tbody>
</table>

From equation, the heat required for evaporation is

\[
Q = 0.0278 \times 3960 (80 - 15) + 0.0209 \times 2309 \times 10^3
\]

\[
= 5.54 \times 10^4 \text{ J s}^{-1}
\]
On the assumption of a heat balance in which the heat supplied by the steam equals the heat required for evaporation,

\[
\text{mass of steam} = \frac{5.54 \times 10^4}{2.36 \times 10^6} = 0.023 \text{ kg s}^{-1} = 34.5 \text{ kg h}^{-1}
\]

To find the number of tubes, we have from equation, \((Q = UA\Delta t)\) that

\[
5.54 \times 10^4 = 2600 \times A (115 - 80)
\]

Therefore

\[
A = 0.61 \text{ m}^2
\]

Now

\[
\text{area of one tube} = 0.025 \times 1.55 \times 3.142 = 0.122 \text{ m}^2
\]

Thus,

\[
\text{number of tubes} = \frac{0.61}{0.122} = 5
\]

**Table 2** Latent heat of vaporisation of water

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Latent heat (Jkg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(2.494 \times 10^6)</td>
</tr>
<tr>
<td>20</td>
<td>(2.448 \times 10^6)</td>
</tr>
<tr>
<td>40</td>
<td>(2.402 \times 10^6)</td>
</tr>
<tr>
<td>60</td>
<td>(2.357 \times 10^6)</td>
</tr>
<tr>
<td>80</td>
<td>(2.309 \times 10^6)</td>
</tr>
<tr>
<td>100</td>
<td>(2.258 \times 10^6)</td>
</tr>
</tbody>
</table>

**Sample problem**

Milk containing 3.7% fat and 12.8% total solids is to be evaporated to a produce a product containing 7.9% fat. What is the yield of product from 100 kg of milk and what is the total solids concentration in the final product, assuming that there are no losses during the process?

**Solution to Sample problem**

\[
\text{Mass of fat in 100 kg of milk} = 100 \times 0.037
\]

If \(Y\) = yield of product:

\[
\text{Mass of fat in the evaporated milk} = Y \times 0.079
\]
As no fat is gained or lost during the process:

\[
0.79 \times Y = 3.7
\]

Yield \((Y) = 46.8 \text{ kg}
\]

<table>
<thead>
<tr>
<th>Mass of solids in the milk</th>
<th>(100 \times 0.128)</th>
</tr>
</thead>
<tbody>
<tr>
<td>If (Z = %) total solids in the evaporated milk</td>
<td></td>
</tr>
<tr>
<td>Solids in the product</td>
<td>(46.8 \times (Z/100))</td>
</tr>
</tbody>
</table>

\[
0.4634 \times Z = 12.8
\]

\[
Z = 27.3\%
\]

**Factors influencing the rate of heat transfer**

The following factors influence the rate of heat transfer and hence determine processing times and the quality of concentrated products:

- **Temperature difference between the steam and boiling liquid.** There are two options to increase the temperature difference: to increase the pressure and temperature of the steam or to reduce the temperature of the boiling liquid by evaporating under a partial vacuum. In commercial vacuum evaporators the boiling point may be reduced to as low as 40°C. However, both methods increase the capital cost of equipment because of the extra strength required, and also the cost of energy needed for processing. The temperature difference becomes smaller as foods become more concentrated, owing to elevation of the boiling point, and the rate of heat transfer therefore falls as evaporation proceeds. In large evaporators, the boiling point of liquid at the base may be slightly raised as a result of increased pressure from the weight of liquid above (the hydrostatic head). In such cases measurement of the boiling point for processing calculations is made half-way up the evaporator.

- **Deposits on heat transfer surfaces.** The ‘fouling’ of evaporator surfaces reduces the rate of heat transfer. It depends on the temperature difference between the food and the heated surface and the viscosity and chemical composition of the food. For example, denaturation of proteins or deposition of polysaccharides cause the food to burn onto hot surfaces. Fouling is reduced in some types of equipment by continuously removing food from the evaporator walls (Section 13.1.2). Metal corrosion on the steam side of evaporation equipment would also reduce the rate of heat transfer, but it is reduced by anti-corrosion chemicals or surfaces. Both types of deposit are described in detail by Pulido (1984).

- **Boundary films.** A film of stationary liquid at the evaporator wall is often the main resistance to heat transfer. The thickness of the boundary film is reduced by promoting convection currents within the food or by mechanically induced turbulence (Section 13.1.2). The viscosity of many foods increases as concentration proceeds. This reduces the Reynolds number and hence reduces the rate of heat transfer. In addition, more viscous foods are in contact with hot surfaces for longer periods and, as a result, suffer greater heat damage.
Factors influencing the economics of evaporation

The main factors that influence the economics of evaporation are loss of concentrate or product quality (Section 13.2) and high energy consumption. Product losses are caused by foaming, due to proteins and carbohydrates in the food, which causes inefficient separation of vapour and concentrate, and entrainment, in which a fine mist of concentrate is produced during the violent boiling, and is carried out of the evaporator by the vapour. Most designs of equipment include disengagement spaces or separators to minimise entrainment.

A substantial amount of energy is needed to remove water from foods by boiling (2257 kJ per kilogram of water evaporated at 100ºC). The economics of evaporation are therefore substantially improved by attention to the design and operation of equipment and careful planning of energy use. Smith (1997) describes an energy management system used in a sugar refinery that has resulted in substantial savings in energy consumption.

Energy can be saved by re-using heat contained in vapours produced from the boiling food by:

- vapour recompression, in which the pressure (and therefore the temperature) of vapour is increased, using a mechanical compressor or a Venturi-type steam jet. The resulting high pressure steam is re-used as a heating medium.
- preheating, in which vapour is used to heat the incoming feed liquor or condensed vapour is used to raise steam in a boiler.
- multiple effect evaporation, in which several evaporators (or ‘effects’) are connected together. Vapour from one effect is used directly as the heating medium in the next.

Table 3 Steam consumption with vapour recompression and multiple effect evaporation

<table>
<thead>
<tr>
<th>Number of effects</th>
<th>Steam consumption (kg per kg of water evaporated)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without vapour recompression</td>
</tr>
<tr>
<td>1</td>
<td>1.1</td>
</tr>
<tr>
<td>2</td>
<td>0.6</td>
</tr>
<tr>
<td>3</td>
<td>0.4</td>
</tr>
</tbody>
</table>


However, the vapour can only be used to boil liquids at a lower boiling temperature. The effects must therefore have progressively lower pressures in order to maintain the temperature difference between the feed and the heating medium.

The number of effects used in a multiple effect system is determined by the savings in energy consumption (Table 3) compared with the higher capital investment required, and the provision of increasingly higher vacua in successive effects (Rumsey et al., 1984). In the majority of applications, three to six effects are used but up to nine effects have been reported (Anon., 1981).
Different arrangements of multiple effect evaporators are shown in Fig. 2 using triple-
effect evaporation as an example and the relative advantages and limitations of each
arrangement are described in Table 4.

Table 4 Advantages and limitations of various methods of multiple effect evaporation

<table>
<thead>
<tr>
<th>Arrangement of effects</th>
<th>Advantages</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forward feed</td>
<td>Least expensive, simple to operate, no feed pumps required between effects, lower temperatures with subsequent effects and therefore less risk of heat damage to more viscous product</td>
<td>Reduced heat transfer rate as the feed becomes more viscous, rate of evaporation falls with each effect, best quality steam used on initial feed which is easiest to evaporate. Feed must be introduced at boiling point to prevent loss of economy (if steam supplies sensible heat, less vapour is available for subsequent effects)</td>
</tr>
<tr>
<td>Reverse feed</td>
<td>No feed pump initially, best-quality steam used on the most difficult material to concentrate, better economy and heat transfer rate as effects are not subject to variation in feed temperature and feed meets hotter surfaces as it becomes more concentrated thus partly offsetting increase in viscosity</td>
<td>Interstage pumps necessary, higher risk of heat damage to viscous products as liquor moves more slowly over hotter surfaces, risk of fouling</td>
</tr>
<tr>
<td>Mixed feed</td>
<td>Simplicity of forward feed and economy of backward feed, useful for very viscous foods</td>
<td>More complex and expensive</td>
</tr>
<tr>
<td>Parallel</td>
<td>For crystal production, allows greater control over crystallisation and prevents the need to pump crystal slurries</td>
<td>Most complex and expensive of the arrangements, extraction pumps required for each effect</td>
</tr>
</tbody>
</table>

Adapted from Brennan et al. (1990).
Fig. 13.2 Arrangement of effects in multiple effect evaporation: (a) forward; (b) reverse; (c) parallel; (d) mixed. (After Brennan et al. (1990).)

Equipment

Evaporators consist of:

- a heat exchanger (termed a calandria) which transfers heat from steam to the food
- a means of separating the vapours produced
- a mechanical or steam ejector vacuum pump. Mechanical pumps have lower operating costs but higher capital costs than steam ejector pumps

Separation in an evaporator is achieved by exploiting the difference in volatility between water and solutes. Ideally it should selectively remove water without changing the solute composition, so that the original product is obtained on dilution. This is approached in some equipment but, the closer to the ideal that is achieved, the higher the cost. As with other unit operations the selection of a particular method is therefore a compromise between the cost of production and the quality required in the product. The selection of an evaporator should include the following considerations:
Energy consumption is a major factor in evaporation, and significant developments have taken place in computer control of evaporators (for example Anon. (1986)). The most widespread evaporators for juice concentration are falling film evaporators (see below) and an example of these is the ‘thermally accelerated short-time evaporator’ (TASTE) (Kennedy et al., 1983). Under manual operation, the steam flow is set at a constant rate and the juice flow is manually adjusted to obtain the required concentration in the final product. This may fluctuate by a several °Brix due to changes in feed composition or other variables in the process and requires skill and experience by the operator to correct the deviation from the required concentration. This results in both off specification products and wastage of energy. 

Chen et al. (1981) describe computer control systems, involving control of steam and juice temperatures and flowrates to improve the economy of TASTE evaporators.

In some applications it may be more cost effective to combine two types of evaporator, for example initial concentration of the bulk liquor in a low cost evaporator followed by final concentration of the smaller volume of heat sensitive liquor in a more expensive, but less damaging evaporator as the second effect. The majority of evaporator designs operate continuously but batch boiling pans are used for the preparation of small quantities of materials, or in applications where flexibility is required for frequent changes of product.

**Natural circulation evaporators**

*Open- or closed-pan evaporators* are hemispherical pans, heated directly by gas or electrical resistance wires or heated indirectly by steam passed through internal tubes or an external jacket. For vacuum operation, they are fitted with a lid. A stirrer or paddle is used to increase the rate of heat transfer and to prevent food from burning onto the pan. They are similar in appearance to jacketed mixing vessels. They have relatively low rates of heat transfer (Table 5) and low energy efficiencies, and they cause damage to heat-sensitive foods. However, they have low capital costs, are relatively easy to construct and maintain and are flexible for applications where frequent changes of product are likely, or when used for relatively low or variable production rates. They have therefore found wide application in the preparation of ingredients such as sauces and gravies or in the manufacture of jam and other preserves (see, for example, Darrington, 1982).

The *short-tube evaporator* is an example of a tube-and-shell heat exchanger, also used in pasteurisation and heat sterilisation. It consists of a vessel (or shell) which contains a vertical, or less commonly horizontal bundle of tubes. The vertical arrangement of tubes promotes natural convection currents and therefore higher rates of heat transfer (Fig. 3). Feed liquor is heated by steam condensing on the outside of the tubes and rises through the tubes, boils and...
recirculates through a central downcomer tube. *External calandria evaporators* are tube-and-shell heat exchangers which are fitted with an external pipe for recirculation of the product. This increases convection currents and rates of heat transfer, and the calandria is easily accessible for cleaning. They are suitable for concentrating heat-sensitive foods, including dairy products and meat extracts, when operated under partial vacuum.

![Diagram of a vertical short-tube evaporator](image)

**Fig. 3** Vertical short-tube evaporator. (After Karel (1975).)

These evaporators have low construction and maintenance costs, high flexibility and higher rates of heat transfer than open or closed pans, when used with relatively low viscosity liquids (Table 5). They are generally unsuited to high-viscosity liquors as there is poor circulation of liquor and a high risk of food burning onto the tube walls. They are used for concentrating syrups, salt and fruit juices.

*Long-tube evaporators* consist of a vertical bundle of tubes, each up to 5 cm in diameter, contained within a steam shell 3–15 m high. Liquor is heated almost to boiling point before entering the evaporator. It is then further heated inside the tubes and boiling commences. The expansion of steam forces a thin film of rapidly concentrating liquor up the walls of each tube (Fig. 4). The concentrate is separated from the vapour and removed from the evaporator, passed to subsequent effects in a multiple-effect system, or recirculated. Vapour is re-used in multiple-effect or vapour recompression systems.

For low-viscosity foods (for example milk), the thin film of liquor is forced up the evaporator tubes and this arrangement is therefore known as a *climbing-film evaporator*. For more viscous foods, or those that are very heat sensitive, (for example yeast extracts, fruit juices (Anon., 1981) and in starch processing), the feed is introduced at the top of the tube bundle in a *falling-film evaporator*. The force of gravity supplements the forces arising from expansion of the steam, to produce very high liquor flow rates (up to 200 ms$^{-1}$ at the end of 12 m tubes) and short residence times (typically 5–30 s). Multiple-effect systems, capable of evaporating 45 000 l of milk per hour, have been described (Anon., 1986). Both types of long-tube evaporator are characterised by high heat transfer coefficients (Table 5) and efficient energy use (0.3–0.4 kg of steam per kilogram of water evaporated in multiple-effect...
systems). Falling film evaporators are now the most commonly used in the food industry and are described in detail by Burkart and Wiegand (1987).

![Climbing-film evaporator](image)

**Fig. 4 Climbing-film evaporator.**

**Forced circulation evaporators**

In forced-circulation evaporators a pump or scraper assembly moves the liquor, usually in thin layers, and thus maintains high heat transfer rates and short residence times (Table 5). This also results in more compact equipment and higher production rates but increases both the capital and the operating costs of the equipment.

**Plate evaporators** are similar in construction to the heat exchangers used for pasteurisation and ultra high-temperature (UHT) sterilisation. However, in this case the climbing- and falling-film principle is used to concentrate liquids in the spaces between plates. The number of climbing- or falling-film sections fitted within a single machine depends on the production rate and degree of concentration required. The mixture of vapour and concentrate is separated outside the evaporator. Despite the high capital investment, these types of evaporator have high rates of heat transfer, short residence times and high energy efficiencies (Table 5). They are compact, capable of high throughputs and easily dismantled for maintenance and inspection. They are more suitable for heat-sensitive foods of higher viscosity (0.3–0.4Nsm⁻²) including yeast extracts, dairy products, fruit juices, low alcohol drinks and meat extracts. Their advantages, compared to other falling film evaporators, are described by Olsson (1988).

The **expanding-flow evaporator** uses similar principles to the plate evaporator but has a stack of inverted cones instead of a series of plates. Feed liquor flows to alternate spaces between the cones from a central shaft and evaporates as it passes up through channels of increasing flow area (hence the name of the equipment). Steam is fed down alternate channels. The vapour-concentrate mixture leaves the cone assembly tangentially and is separated by a special design of shell which induces a cyclone effect. This evaporator has a
number of advantages including compactness, short residence times and a high degree of flexibility achieved by changing the number of cones.

**Mechanical (or agitated) thin-film evaporators**

*Scraped- or wiped-surface evaporators* are characterised by differences in the thickness of the film of food being processed. Wiped-film evaporators have a film thickness of approximately 0.25mm whereas in scraped-film evaporators it is up to 1.25 mm. Both types consist of a steam jacket surrounding a high-speed rotor, fitted with short blades along its length (Fig. 5). The design is similar to a scraped-surface aseptic steriliser. Feed liquor is introduced between the rotor and the heated surface and evaporation takes place rapidly as a thin film of liquor is swept through the machine by the rotor blades. The blades keep the film violently agitated and thus promote high rates of heat transfer and prevent the product from burning onto the hot surface (Anon., 1981). The residence time of the liquor is adjusted between 0.5 s and 100 s depending on the type of food and the degree of concentration required.

This type of equipment is highly suited to viscous (up to 20Nsm⁻²) heat-sensitive foods or to those that are liable to foam or foul evaporator surfaces (for example fruit pulps and juices, tomato paste, meat extracts, honey, cocoa mass, coffee and dairy products). However, the capital costs are high owing to the precise alignment required between the rotor and wall. Operating costs are also high as only single effects are possible, which reduces the throughput and gives poor steam economy. It is therefore used for ‘finishing’ highly viscous products after concentration in other equipment where there is less water to be removed, the product is valuable and there is a substantial risk of heat damage.

A second design of mechanical thin-film evaporator is the *Centri-therm evaporator* which, although similar in appearance to the expanding flow evaporator, operates using a different principle. Here, liquor is fed from a central pipe to the undersides of rotating hollow cones. It immediately spreads out to form a layer approximately 0.1mm thick. Steam condenses on the other side of each cone, and rapidly evaporates the liquor. In contrast with the expanding-flow evaporator, in which liquid is moved by vapour pressure, the Centri-therm employs centrifugal force to move the liquor rapidly across the heated surface of the cone.
Residence times are 0.6–1.6 s (Lewicki and Kowalczyk, 1980), even with concentrated liquors (up to 20Nsm\(^{-2}\)). Very high heat transfer coefficients and short residence times are possible (Table 5). This is due in part to the thin layers of liquor but also to the droplets of condensed steam which are flung from the rotating cones as fast as they are formed. There is therefore no boundary film of condensate to impede heat transfer. The equipment produces a concentrate which, when rediluted, has sensory and nutritional qualities that are virtually unchanged from those of the feed material. It is used for coffee and tea extracts, meat extract, fruit juices (Fischer \textit{et al}., 1983) and enzymes for use in food processing.

**Table 13.5** Comparison of residence times and heat transfer coefficients in selected evaporators

<table>
<thead>
<tr>
<th>Type of evaporator</th>
<th>Number of stages</th>
<th>Residence time (approximate)</th>
<th>OITC (Wm(^{-1})K(^{-1})) Low viscosity</th>
<th>OITC (Wm(^{-1})K(^{-1})) High viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Open or vacuum pan</td>
<td>Single</td>
<td>30 min to several hours</td>
<td>300–1000</td>
<td>&lt; 300</td>
</tr>
<tr>
<td>Vertical short tube</td>
<td>Single</td>
<td>–</td>
<td>570–2800</td>
<td>–</td>
</tr>
<tr>
<td>Climbing film</td>
<td>Single</td>
<td>10–60 sec</td>
<td>2230–6000</td>
<td>&lt; 300</td>
</tr>
<tr>
<td>Falling film</td>
<td>Single</td>
<td>5–30 sec</td>
<td>2000–3000</td>
<td>–</td>
</tr>
<tr>
<td>Plate</td>
<td>Three</td>
<td>2–30 sec</td>
<td>2000–3000</td>
<td>–</td>
</tr>
<tr>
<td>Expanding flow</td>
<td>Two</td>
<td>0.5–30 sec</td>
<td>2500</td>
<td>–</td>
</tr>
<tr>
<td>Agitated film</td>
<td>Single</td>
<td>20–30 sec</td>
<td>2000–3000</td>
<td>1700</td>
</tr>
<tr>
<td>Centri-Therm</td>
<td>Single</td>
<td>1–10 sec</td>
<td>8000</td>
<td>–</td>
</tr>
</tbody>
</table>

Adapted from Maunheim and Passy (1974) and Earle (1983).

**Effect on foods**

Aroma compounds that are more volatile than water are thus lost during evaporation. This reduces the sensory characteristics of most concentrates; in fruit juices this results in a loss of flavour, although in some foods the loss of unpleasant volatiles improves the product quality (for example in cocoa (Anon., 1981) and milk). Some volatiles can be recovered and retained in the product:

- by volatile recovery by vapour condensation and fractional distillation
- by stripping volatiles from the feed liquor with inert gas and adding them back after evaporation

The advantages and limitations of each procedure have been reviewed by Mannheim and Passy (1972) and Thijssen (1970). Flash coolers, in which the food is sprayed into a vacuum chamber, are used to cool a viscous product rapidly and hence to reduce heat damage.

Evaporation darkens the colour of foods, partly because of the increase in concentration of solids, but also because the reduction in water activity promotes chemical changes, (for example Maillard browning). As these changes are time and temperature dependent, short residence times and low boiling temperatures produce concentrates which have a good retention of sensory and nutritional qualities. A comparison of nutrient losses in milk preserved by evaporation and UHT sterilisation is shown in Table 13.6. Vitamins A and D and niacin are unaffected. Additional vitamin losses occur during storage (for example 50%
loss of vitamin C in marmalade over 12 months at 18°C (Lincoln and McCay, 1945) and 10% loss of thiamin over 24 months in peanut butter at 18°C).

Table 6 Vitamin losses in concentrated and UHT sterilised milk

<table>
<thead>
<tr>
<th>Product</th>
<th>Thiamin</th>
<th>Vitamin B&lt;sub&gt;6&lt;/sub&gt;</th>
<th>Vitamin B&lt;sub&gt;12&lt;/sub&gt;</th>
<th>Folic acid</th>
<th>Ascorbic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporated milk</td>
<td>20</td>
<td>40</td>
<td>80</td>
<td>25</td>
<td>60</td>
</tr>
<tr>
<td>Sweetened condensed milk</td>
<td>10</td>
<td>&lt;10</td>
<td>30</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>UHT sterilised milk</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;25</td>
</tr>
</tbody>
</table>

From Porter and Thompson (1976).

References:

1. 4 Development of a model for quality assessment of tomatoes and apricots

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Abstract

The quality of tomato and apricot cultivars was assessed by sensory evaluation, consumer tests and instrumental methods.

The overall sensory appreciation of tomatoes was mainly reflected by attributes such as “sweetness”, “aroma”, “juiciness” and “firmness”. Hedonic classification of samples allowed to significantly improve the correlation between instrumental data and consumer appreciation. Instrumental measurements were focused on total sugar content (1Brix) and total amount of volatile compounds and texture (firmness). For tomatoes the CAR/PDMS fibre and for apricots the PDMS fibre were used for the analysis of total volatiles.

The results obtained with tomatoes and apricots confirmed the applicability of the quality assessment model developed for evaluation of the quality of strawberries.

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Keywords: Tomatoes; Apricots; Quality assessment; SPME; Total volatile compounds; Sensory evaluation

1. Introduction

Attributes such as colour, size, shape and external defects of fruit and vegetables predominantly determine the choice made by the consumers. However, these parameters alone do not guarantee the flavour and texture quality of a product. The sum of sugars, organic acids and the amount of volatile compounds, as well as colour, shape and texture determine the sensory properties of fruit and vegetables, e.g. tomatoes and apricots (Resurrection & Shewfelt, 1985; Parolari, Virgili, Bolzoni, Careri, & Mangia, 1992a; Parolari, Virgili, & Bolzoni, 1992b; Porretta, 1993).

The flavour of tomatoes and apricots can be characterized by nearly the entire set of their constituents. Indeed, the flavour is not only directly reflected by the sum of the volatile and nonvolatile components, but also depends on their interactions (Kavanagh & McGlasson, 1983; Petro-Turza 1987; Parolari et al., 1992). Although taste and odour are perceived by different senses, the proximity of these senses and their connection through the pharynx render separate analyses of taste and odour difficult.

Sugars and acids reflect the overall taste preference for a fruit. Over the past decades research has been carried out to enhance the sugar and acid contents, thereby acting on the pleasant sweet–sour taste of the fruit. The sugar fraction of tomatoes is essentially composed of glucose and fructose. Taste character and intensity are greatly affected by salts and by the buffering effect of the cations and anions present. The incidence of the sugar/acid ratio has been shown to be of little/no importance for tomatoes (Stevens, Kader, Albright-Holten, & Algazi, 1977; Kader, Morris, Stevens, & Albright-Holten, 1978).

So far, only little attention has been paid to the contribution of the volatile compounds to the quality of tomatoes. Although more than 400 volatile compounds have been identified, only few of them such as hexanal, (E)-2-hexenal, (Z)-3-hexenal, (Z)-3-hexenol, (E)-2-(E)-4-decadienal, 2-isobutylthiazole, 6-methyl-5-hepten-2-one, 1-penten-3-one and b-ionone seem to play an important role for the flavour of tomatoes (Buttery, Seift, Guadagni, & Ling, 1971; Ho & Ichimura, 1982; Buttery, Teranishi, & Ling, 1987; Petro-Turza 1987; Buttery, Teranishi, Ling, & Flath, 1988; Ulrich, Krumbein, & Rapp, 1997). 2-Isobutylthiazole is present in very small amounts; however, its concentration increases rapidly during mastication of the tomato in the mouth. On the
other hand, hexanal and (E)-2-hexenal is produced in mashed tissue by an enzymatic lipid oxidation. Hexenol is formed by the action of alcohol dehydrogenase on hexenal (Linforth & Taylor, 1996). Butterey et al. (1987), Butterey, Teranishi, Ling, and Turabaugh (1990) provide a scientific basis for the subjective observation that cold storage is deleterious to fresh tomato flavour. The same authors have proposed amixture of substances to match the typical aroma of a tomato paste. Only few reports with analytical data thorough enough to be useful for quality control of apricots are available (Gherardi, Poli, & Bigliardi, 1978; Blandau et al., 1985; Monastero, Deutsch, & Ellero, 1992; Lo Voi, Impembo, Fasanaro, & Castaldo, 1995). The first studies on apricot flavour were performed by Tang & Jennings (1968); a number of terpenes and alcohols were identified to be present in the “Blenheim” cultivar. Several constituents, such as lactones, terpene alcohols and benzaldehyde were identified in different apricot cultivars (Bernreuther & Schreier, 1991; Chairote, Rodriguez, & Crouzet, 1981; Rodriguez, Seck, & Crouzet, 1980). Guichard & Souty (1988) compared the relative concentrations of various volatiles in six different apricot cultivars, and showed the C6 lipid degradation products, lactones, terpenes and ketones to be the most abundant constituents. Odour unit values and odour threshold data indicated that volatile compounds such as β-ionone, linalool, g-decalactone, hexanal, (E)-2-hexenal, (E,E)-decadienal, (E)-2-nonenal and g-dodecalactone represented the major contributors to the apricot aroma (Takeoka et al., 1990).

On the other hand, the quantitative composition of organic acids and soluble sugars have often been used as indicators for the quality of apricots (Parolari et al., 1992; Bartolozzi, Bertazza, Bassi, & Cristoferi, 1997). Recently, GC-MS was used to evaluate sugars, sugar alcohols, acids and amino acid derivatives, based both on the total ion current (TIC) and selective fragment ion (SFI) values (Katona, Sass, & Molnar-Perl, 1999).

The study of polyphenols is also important because of their contribution to the sensory quality of fruits (colour, astringency, bitterness and flavour) (Herrmann 1990). Analysis of phenolic constituents including the flavonoids allowed to characterize and differentiate apricot cultivars (M. oller & Herrmann, 1983; Fernandez de Simon, P’erez-Izarbe, Hernandez, Gomez-Cordoves, & Estrella, 1992; Garcia-Viguer, Bridle, Ferreres, & Tomas-Barberan, 1994).

The present work describes the application of a new concept developed for quality assessment of strawberries (Azodanlou, Luisier, Villettaz, Darbellay, & Amad’o, 2003), to evaluate the quality of tomatoes and apricots. The total amounts of volatile compounds of tomatoes and apricots were determined by the method of Azodanlou, Luisier, Villettaz, and Amad’o (1998), Azodanlou, Darbellay, Luisier, Villettaz, and Amad’o (1999a, b). Sensory evaluation and physico-chemical instrumental methods have been used as complementary tools to determine and to set quality acceptance limits.

2. Materials and methods

2.1. Fruit samples and sample preparation

2.1.1. Tomatoes

During three growing seasons (1997, 1998, 1999) 149 samples representing 28 tomato cultivars, grown on field, in glasshouses or in plastic tunnels were harvested at the ripe stage and used immediately for sensory evaluation and instrumental analyses. The fruits were obtained either from the Swiss Federal Research Station for Plant Production in Conthey (Switzerland) or from a large food retailer (Federation of Migros Cooperatives, Bussigny, Switzerland). The tomatoes were harvested at different periods in June and July.

2.1.2. Apricots

Consumer tests and instrumental analyses with apricots were carried out in 1999 on the cultivars Jumbo, Luiset, Bergeron, Fantasme and Tardif de Tain. The apricots were obtained from the local Research Station for Fruit Production (Châteauneuf, Switzerland), and were harvested at two or three different stages of ripeness: pre-ripe (near to ripe), ripe and over-ripe.

Intact fruits were used for sensory evaluation and for determination of total volatile compounds.

Tomatoes and apricots classified by sensory evaluation were homogenized at high speed either in a Solemio blender (Fiseldem, Cinisello, Italy) or in a professional blender (Kenwood, USA) for approximately 30 s to produce a homogeneous purée which was directly used for instrumental analyses. To inactivate the endogenous enzymes, 50 g of a saturated ammonium sulphate (purum, Fluka AG Buchs, Switzerland) solution was added to 50 g of fruit, directly into the blender. Finally, 2-methyl-1-pentanol (purum, Fluka; 1 mg/100 g of homogenate) was added as internal standard.

2.2. Sensory evaluation

2.2.1. Consumer tests

Approximately 120 consumers participated in a hedonic test performed in supermarkets (Federation of Migros Cooperatives) in different Swiss cities (Bern, Lausanne, St. Gallen, San Antonino, Sion,
The test persons were asked to give an overall appreciation of tomatoes and apricots on a 1–9 liking scale: 1=extremely bad to 9=extremely good. The overall appreciation is the only attribute that confirms the quality of the product. In the 1999 campaign a modified procedure was adopted. Each fruit was divided into halves; one half was used to assess for the sensory quality, while the other half was assigned to different baskets according to the score obtained (1–9). The pooled samples were homogenized as described above and used for instrumental analyses. This way of classifying samples is hereafter called “hedonic classification”.

To improve quality assessment, the hedonic classification was applied to the tomatoes and apricots as described in a previous work (Azodanlou et al., 2003) for strawberries.

2.2.2. Sensory panel

The sensory panel consisted of 10–15 semi-trained subjects. Each panellist received between 10 and 15 samples, then the panel rated the different parameters on a 1–9 scale (e.g. 1=very weak aroma intensity and 9=very strong aroma intensity). The same liking scale was used for the overall appreciation (extremely bad to extremely good). Panellists were given water (Volvic, Puy-de-Dome, France) as neutralizing beverage between sample testing. The evaluation was carried out in a standard sensory laboratory under well-controlled conditions using red light to mask any colour differences.

The subjects were asked to rate the following sensory attributes: odour, aroma, sweetness, acidity, skin hardness, flesh firmness, juiciness, mealiness and to give their overall appreciation.

2.3. Instrumental analyses

2.3.1. Determination of total volatile compounds

Fresh intact tomatoes or apricots (40071 g) were carefully placed in a 6L headspace flask with wide opening (NS 160/100). For the measurements on puree, 10071 g of the homogenate were spread out in a crystallising dish (10 cm diameter, 3 cm high) which was placed in the headspace flask. The analyses were carried out using the same types of SPME fibres as described in a previous work (Azodanlou et al., 2003) and the experimental procedure was strictly followed:

Different types of SPME fibres were used: polydimethylsiloxane (PDMS) with 100 mm thickness (Cat No. 5-7300-U); polycrylate (PA) 85 mm (Cat. No. 5-7304); porous fibres Carbowax/divinylbenzene (CW/DVB), 65 mm (Cat. No. 5-7312); bi-polar fibres: PDMS/DVB 65 mm (Cat. No. 5-7310-U), Carboxen-PDMS (CAR/PDMS) 75 mm (Cat. No. 5-7318) and CW/CAR/PDMS 50/30 mm (5-7328-U) all obtained from Supelco Co. (Bellefonte, PA).

The fruits were left for 5 min at 251C to obtain the necessary gas equilibrium in the headspace. Aliquots of the volatile compounds were then collected by inserting the SPME needle through a teflon-coated silicone septum into the headspace of the flask. After 5 min (sampling time) the adsorbed substances were desorbed into a gas chromatograph HRGC-5300 (Carlo Erba S.p.A., Milano, Italy) equipped with a splitless injector port, directly coupled to the flame ionization detector, using a transfer tube (20 cm in length, 0.1mm i.d., N1160–2630, J&W, New Brighton, MN). The following GC conditions were used:

- helium carrier gas pressure 150 kPa at a flow rate of approx. 5 mL/min;
- hydrogen and air pressure for the FID: 50 and 80kPa, respectively;
- oven temperature 2501C;
- injection port and the detector temperatures 2001C and 2501C, respectively.

A mixture (3 mg/kg) of 1-methoxy-2-propylacetate (Merck, for synthesis), 2-methyl ethyl ketone (Fluka, purum), and butanol (Fluka, puriss.) was used as external standard. The total volatile peak (mVmin) was measured with a Borwin integrator (JMBS Developpements, Grenoble, France). Between each analysis, the headspace flask was cleaned by purging with filtrated air that had previously passed through a charcoal trap (Supelpure-HC Trap, Supelco Co).

Measurements on fruit puree were carried out by spreading the sample into a crystallizing dish (10 cm diameter, 3 cm height) which was then placed in the 6L headspace flask. Total analysis time was approximately 15 min, including 5 min for both equilibration and sampling. Each sample was analysed in triplicate.

2.3.2. Identification and quantification of volatile compounds in tomatoes and apricots

The volatile compounds of tomatoes and apricots were extracted by SPME (CAR/PDMS) and identified and quantified by GC. The volatiles present in the headspace (250 mL) were analysed using the same procedure as described before (Azodanlou et al., 2003).

Identification was performed by a combination of Kovats retention indices and a GC-MS library (Flavornet, Geneva, USA). Some components were identified by comparison of retention time and mass spectra with authentic substances. The following
reference substances were used: hexanal, butyl acetate, (Z)-3-hexenol, 3-methyl-1-pentanol, (E)-2-hexenol, hexanol, 2-heptanone, butyl butanoate, hexenyl acetate, 2,6-dimethyl-6-hepten-2-ol, 1-octanol, propyl hexanoate, linalool, isobutyl hexanoate (Fluka); isoamyl acetate, (E)-2-(E)-4-decadienal (Aldrich, Milwaukee, USA); dimethyl disulfide, (E)-2-hexenal, methional, 6-methyl-5-hepten-2-one, n-hexenyl propanoate, butyl hexanoate, pentyl hexanoate, hexyl hexanoate, a-ionone, g-decalactone (Givaudan-Roure, Dübendorf, Switzerland). The same procedure was adopted as described by Azodanlou et al. (2003).

2.3.3. Determination of total sugar content and total acidity

Tomato and apricot puree (20071 g) were used for these analyses. Total sugar content (1Brix) was determined using a refractometer (Atago, PR-1, Tokyo, Japan). pH and total acidity were measured with a titrator (Mettler DL 25, Mettler-Toledo, Greifensee, Switzerland). For determination of total acidity, 1070.1 g of sample was titrated to pH 8.0 using 0.1 mol/L NaOH. The titrated volume (mL) corresponds directly to total acidity expressed as g/L citric acid.

2.3.4. Texture analysis

The firmness of the fruits (10071 g) was determined either using a penetrometer (PNR 20 Benchtop Loud & Tensile Tester, Petrolab Co., Latham, USA) fitted with a round or a conic head or a Kramer’s shear cell operated by a shear test machine (VersiTest-Advanced Forces Gauge, Memesin, Br. utsch & R.uegger, Zurich, Switzerland). The device speed was set at 250 mm/min. The fruits were divided into four parts prior to measurements which were performed in triplicate, at ambient temperature.

2.3.5. Conductivity and mineral components analysis

The conductivity was measured directly on the tomato and apricot paste using a Metrohm 660 conductimeter (Metrohm AG, Herisau, Switzerland). For the quantitative analysis of Na, K, Mg, and Ca, the puree was first centrifuged at 30,000 g for 10 min at room temperature. Aliquots of the supernatant were analysed by inductively coupled plasma emission spectroscopy (ICP-ES 400, Perkin Elmer, Palo Alto, USA).

2.4. Statistical evaluation

The Statview program (Abacus concepts Inc., Berkeley, USA) was used for the analysis of variance (ANOVA). Significant differences in instrumental measurements among samples were determined by protected least significant difference (PLSD) with P≤0:05: Where the test of normality failed, the nonparametric test was applied to the individual panel scores for every investigated intensity criteria and then transformed into ranking numbers. The nonparametric test was processed by the Kruskall & Wallis test (P≤0:05). The Statbox program (Grimmer Logiciels Corp., Paris, France) was used for the Pearson’s correlation (P≤0:05) and the principal component analysis (PCA) carried out to identify the interdependence between different cultivar and ripening stage.

3. Results and discussion

The aim of this study was to evaluate the applicability of the quality assessment system developed for strawberries (Azodanlou et al., 2003) on tomatoes and apricots. The quality of tomatoes was investigated through the years 1997, 1998 and 1999, whereas the experiments with apricots were limited to 1999 only. In a first step, the sensory panel was used to define quality attributes. Then, samples were judged by consumers and the relationship between sensory and instrumental data was investigated. Finally, a model for quality assessment of tomatoes and apricots was proposed.

3.1. Quality assessment of tomatoes

3.1.1. Sensory evaluation

A sensory panel was used to set up quality descriptors (Azodanlou, 2001). Of the 28 cultivars, 149 tomato samples were used for the identification of the most important quality attributes. Because the normality test failed (large variance of the results), the nonparametric test was used. In 1997 the objective of the panel was to define descriptors for the sensory quality of tomatoes (Table 1). Aroma, sweetness, skin hardness as well as flesh firmness, juiciness and mealiness were shown to be statistically relevant, whereas the attributes herbaceous odor and salty taste were not relevant (low significance: P > 0:05). Although mealiness turned out to be an important quality criterion, its instrumental determination was unfortunately not possible because of lack of a suitable device.

Most of the descriptors found to be significant in 1997 have been confirmed during the 1998 and 1999 campaigns (Table 1). The results allowed to define “aroma”, “sweetness”, “skin hardness”, “flesh firmness” and “juiciness” to be significant attributes to describe the quality of tomatoes.

Thirty samples were tested by consumers in 1998 and 1999. The results made clear that the overall
appreciation by a hedonic test was highly significant (Table 1). The large number of fruits needed for the consumer tests (n = 120) led to abstain from a complete covering of this type of sensory evaluation (n = 10-15). Instead, the sensory panel was asked to give an overall appreciation of the fruits. Out of the defined sensory descriptors, only “juiciness” correlated significantly with the overall appreciation over a 2-year period (P ≤ 0.01; r = 0.54 for 1998 and r = 0.68 for 1999, respectively). The overall appreciation by the consumers correlated well with a few of the quality attributes established by the sensory panel, but for most of the attributes no significant correlation was found (Table 2). The heterogeneity of the fruit samples was thought to be responsible for these results. Nevertheless, consumer tests and instrumental data have been regarded to be appropriate to give reliable information on the quality of tomatoes.

Table 2 shows the low reproducibility of the measurements that made it difficult to find significant correlations. Nevertheless it was possible to retain odour and sweetness as important quality descriptors for tomatoes. It is of particular interest to point out that both descriptors can be determined by instrumental methods (total sugar content and amount of total volatile compounds).

### 3.2. Correlation between sensory and instrumental data

Several chemical and physico-chemical parameters were measured by instrumental methods. The sugar content (1Brix), pH, total acidity, cations (Na, K, Ca, Mg) and firmness data were obtained for tomatoes of all harvests (1997, 1998 and 1999). The amounts of total volatile compounds were determined for the fruits of the 1998 and 1999 seasons.

![Image](image_url)

Relationships between data obtained by consumer tests and instrumental methods have been established. A good correlation was found between total volatile compounds (TV) and the overall appreciation (Fig. 1A). Using the SPME fibres CW/DVB and PDMS correlation factors of r = 0.82 and 0.65 were determined at the P < 0.05 significance level. Experiments carried out with fruits from the 1999 harvest gave a much lower correlation (r = 0.11 and 0.25; respectively, P > 0.05). On the other hand, the total sugar content correlated significantly (P < 0.05) with the overall appreciation by the consumers (r = 0.45) in the 1999 campaign (Fig. 1B). In the 1998 harvest, the correlation was less evident (r = 0.22). The difficulty to reproduce the correlation was probably due to a higher heterogeneity of fruit samples in total volatile compounds and total sugar content (°Brix).

Table 3 summarizes the results of the comparison between the consumer appreciation and the instrumental data. The correlation between the total sugar content and the overall appreciation on the one side and between the amount of total volatile compounds (measured with some of the SPME fibres) and the overall appreciation on the other hand, led to the conclusion that the two attributes “sweetness” and “aroma” are determinant for the quality of tomatoes.

### 3.3. Hedonic classification for the assessment of tomato quality

The main problem in the development of a model for the assessment of the quality of fruits was the heterogeneity of the fruit samples, as demonstrated in a previous work (Azodanlou et al., 1999a). Introduction of the “hedonic classification” (Azodanlou et al., 2003) successfully solved this problem. Indeed, the same fruit sample could be analysed by instrumental methods and by the consumer, which made a direct comparison of the results possible.
3.3.1. Total amount of volatile compounds

Using the ‘hedonic classification’ a good correlation between the total amount of volatile compounds and the consumers’ overall appreciation was found for nearly all SPME fibres used (P≤0.05; r = 0.87-0.98), except for the PA fibre (P≤0.05; r = 0.10), compared to correlations of r = 0.10-0.25 prior to classification. Only the CAR/PDMS fibre showed a linear relationship between the consumers’ appreciation and total volatile compounds (r = 0.98) using hedonically classified tomatoes (Fig. 2A).

In spite of good correlations obtained with other fibres, the large variance of the results increased the difficulty to differentiate between tomatoes of different classes of quality (values not shown).

3.3.2. Tomato aroma compounds

The aroma of the tomato is composed of a large number of substances belonging to different classes of chemicals such as esters, alcohols and carbonyl compounds (Buttery et al., 1987, 1988; Ho & Ichimura, 1982; Kader et al., 1978; Petro-Turza, 1987). These substances contribute to the fruity and green notes (herbaceous odour) of tomatoes and were identified and quantified by GC-MS and GC-FID. Taking into account the results obtained for total volatile compounds, where it was shown that the different types of SPME fibres adsorbed the same substances, however in different amounts, the GC-analyses were carried out with one SPME fibre type only. The CAR/PDMS fibre was chosen because of its good differentiation ability.

<table>
<thead>
<tr>
<th>Instrumental data</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total sugar content</td>
<td>NA</td>
</tr>
<tr>
<td>Total acidity</td>
<td>NA</td>
</tr>
<tr>
<td>pH</td>
<td>NA</td>
</tr>
<tr>
<td>Pheromone</td>
<td>NA</td>
</tr>
<tr>
<td>Kerman’s shear cell</td>
<td>NA</td>
</tr>
<tr>
<td>Conductivity</td>
<td>NA</td>
</tr>
<tr>
<td>Mg content</td>
<td>NA</td>
</tr>
<tr>
<td>Ca content total volatile compounds</td>
<td>NA</td>
</tr>
<tr>
<td>CAR/PDMS</td>
<td>NA</td>
</tr>
<tr>
<td>PDMS/DVB</td>
<td>NA</td>
</tr>
<tr>
<td>CW/DVB</td>
<td>0.81*</td>
</tr>
<tr>
<td>PA</td>
<td>NA</td>
</tr>
<tr>
<td>CAR/PDMS/DVB</td>
<td>NA</td>
</tr>
</tbody>
</table>

*Significant at P≤0.05. NA: not analysed; NS: not significant.
between the scores 1–3 and 7–9 in the overall appreciation (Fig. 2A). As expected, summing up the peak areas measured by GC-FID gave a higher total amount of volatile compounds when compared to the results obtained with the method used to determine the total volatile compounds. GC-FID was clearly more sensitive than the measurement of total volatile compounds.

From the results obtained by the GC-FID method it can be stated that esters contribute essentially to the overall appreciation of tomatoes (r = 0.88). Among the ester group, butyl hexanoate (r = 0.71) was shown to play a major role for the volatiles of tomatoes. In the group of carbonyl compounds (E)-2-hexenal (r = 0.74), 6-methyl-5-hepten-2-one (r = 0.58) and geranyl acetone (r = 0.84) seem to be important. Finally, the sulphur compound 2-isobutylthiazole (r = 0.83) also showed a good correlation with the consumers’ appreciation.

However, a weak correlation was obtained between the sum of volatile compounds determined by GC-FID and the consumers’ overall appreciation (r = 0.46), whereas a much better correlation (r = 0.98) was obtained between the total amount of volatile compounds and the consumers’ appreciation.

Therefore the determination of the total amount of volatile compounds has been selected as the method of choice. Although this method of analysis was less sensitive compared to the summing up of the peak areas measured by GC-FID, it reflects the overall appreciation of the consumers much better.

3.3.3. Total sugar content

A very strong relationship (r = 0.98; P≤0.05) between total sugar content (°Brix) after hedonic classification of the samples and consumers’ appreciation was established as shown in Fig. 2B. Here again the advantage of the hedonic classification was evident, without hedonic-classification the correlation was much lower (r = 0.43).

A good correlation was also found between the consumer ratings and total acidity (r = -0.90) when the tomatoes were hedonically classified. Without hedonic classification r = 0.20 was obtained.

On the whole, the hedonic classification of the samples allowed to substantially enhance the correlation between instrumental data and the consumers’ overall appreciation of tomatoes.

3.4. Development of a model for the assessment of tomato quality

Based on these results we decided to apply the model developed for assessment of strawberry quality (Azodanlou et al., 2003) to tomatoes as well. Three quality levels “bad”, “medium” and “good” were fixed. The average appreciation for “bad” samples was 2 (range: 1–3), for “medium” samples 5 (range: 4–6) and for “good” samples 8 (range: 7–9). In Table 4 intervals and limit values for the different quality attributes as well as sample distribution are given.

Determinations of the amount of total volatile compounds using the CAR/PDMS fibre, and of the total sugar content would allow to predict the quality of tomatoes at harvest. By measuring the amount of total volatile compounds and the total sugar content it was possible to predict the quality of tomatoes at harvest. An overlap between average values for “bad”, “medium” and “good” samples was observed for all other instrumental parameters.

Nevertheless it can be stated that the model developed for the assessment of strawberry quality can be used for tomatoes as well, although the results were not as convincing as for strawberries. Further work remains to be done to improve the system.
3.5. Quality assessment of apricots

The hedonic classification was also applied on apricots, sorted out in three quality classes “bad”, “medium” and “good”.

3.6. Assessment of five apricot cultivars by consumer tests

Five cultivars Jumbo, Fantasme, Bergeron, Luiset, and Tardif de Tain harvested at different stages of maturity were analysed in 1999 by consumer preference tests. Results obtained were treated by PCA. It was interesting to note that 77% of the variability could be explained by the two principal components (Fig. 3). The results clearly demonstrated that principal component analysis allowed to discriminate between different stages of ripeness of Luiset and Jumbo cultivars. Jumbo, Fantasme and Bergeron obtained the best-appreciated score. The consumers disliked the nonfully ripe fruits.
3.7. Hedonic classification for the assessment of apricot quality

3.7.1. Total amount of volatile compounds

A good and statistically significant ($P \leq 0.05$) correlation was found between the total amount of volatile compounds and the consumers’ overall appreciation for the SPME fibres PDMS ($r = 0.93$), CAR/PDMS/DVB ($r = 0.87$) and CAR/PDMS ($r = 0.80$). As an example, the relationship between total volatile compounds (mg/kg) extracted by the PDMS ($r = 0.93$) fibre and the overall appreciation by the consumers using hedonically classified apricots is shown in Fig. 4A.

Two curve shapes were observed for the two sample lots obtained at different harvest dates. This could be explained by the presence of more pre-ripe apricots in the 22.7.1999 harvest date.

3.7.2. Total sugar content

A nonlinear relationship was established between total sugar content (1Brix) with hedonic classification of the samples and consumer appreciation as shown in Fig. 4B ($r = 0.90; P \leq 0.05$). In this case, the differences between the two harvest dates were not significant and had no consequence on the shape of the curves.

Total acidity plays a minor role compared to the sugar content. The correlation was $r \geq 0.53$ between the consumer ratings and total acidity and become stronger with the ratio total acidity/°Brix ($r = -0.92$).

3.7.3. Texture analysis

A good correlation ($r = -0.78$) between texture data as measured by the Kramer’s shear cell and the overall appreciation after hedonic classification was obtained as shown in Fig. 4C. In contrast to the results obtained with tomatoes, firmness played an important role in the appreciation of the quality of apricots.

3.8. Development of a model for the assessment of apricot quality

The hedonic classification allowed to obtain a clearer distinction between the three different quality classes. A model for assessment of apricot quality can therefore be proposed (Table 5).
With respect to the determination of total volatiles only the PDMS fibre allowed to distinguish between the three quality classes. On the other hand, the total sugar content was shown to be a very good parameter to distinguish between the three quality levels, whereas firmness allow a distinction between “bad” and “medium–good” quality.

No significantly differing results were obtained for the other instrumental data and the average values for “bad”, “medium” and “good” quality samples (values not shown).

4. Conclusions

Sweetness and aroma were shown to be the most important quality attributes for tomatoes and apricots. In contrast to the results obtained with tomatoes, firmness allowed to reject the “bad” apricots.

A hedonic classification of the samples allowed us to improve significantly the correlation between instrumental data and consumer overall appreciation and enabled us finally to propose a model for the assessment of the quality of tomatoes and apricots. Multiple variable analysis enabled us to discriminate between quality classes. For the determination of the amount of total volatile compounds the appropriated SPME fibre had to be used. For tomatoes the CAR/PDMS fibre and for apricots the PDMS fibre allowed to distinguish between the three quality classes.

The total sugar content was shown to be a very good parameter to distinguish between the three quality levels of both fruits, whereas texture measurements (firmness) allowed a distinction between the “bad” samples and the other classes of apricots.

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References


**1. 5 Lycopene content of tomato products and their contribution to the lycopene intake of Croatians**

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Abstract

In spite of the interest in the role of lycopene in the prevention of chronic diseases, little is known about the lycopene content of the tomatoes and tomato products commonly consumed in Croatia, and the contribution of these products to the intake of lycopene. The lycopene content of tomatoes and different tomato products was determined. The lycopene content of tomato-based foods was provided to 3 young population groups of Croatia (approximately 1000 nursery children aged 2-6 years, 600 school children aged 6-14 years, and 700 university students aged 18-24 years) in the institutional food service (nursery, school, and university cafeterias), and the daily cafeteria meal intake of lycopene in these populations were estimated. Lycopene content in 24 samples of fresh tomatoes ranged from 1.82 to 11.19 mg per 100 g wet weight. In the 82 brands of different tomato products (tomato puree, ketchup, concentrated tomato paste, tomato juice, and whole canned tomatoes) from markets in Zagreb, Croatia, the values for lycopene content ranged from 3.80 to 52.20 mg per 100 g wet weight for individual samples and from 8.10 to 26.46 mg per 100 g wet weight for average content of various tomato products. The estimated daily cafeteria meal intake of lycopene (from tomatoes and tomato products) was 4.82 mg in nursery children, 4.11 mg in school children, and 3.35 mg in university students. These results have implications for the evaluation of the daily intake of lycopene in Croatia and raise important questions for establishing a recommendation for optimal daily lycopene intake.

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Keywords: Dietary intake; Lycopene; Lycopene content; Tomato; Tomato products

1. Introduction

Lycopene, the pigment principally responsible for the characteristic deep-red color of ripe tomato fruits and tomato products, has received much attention in recent years because of its beneficial effect in the treatment of diseases [1,2]. Lycopene is an acyclic carotenoid and contains 11 conjugated double bonds. Carotenoids are important plant pigments found in the photosynthetic pigment-protein complex of plants, photosynthetic bacteria, fungi, and algae. In nature, most carotenoids originally occur in the all-trans form. However, because of the high number of double bonds, carotenoids can undergo trans to cis isomerization if exposed to light within their absorption range. Interconversion can also be induced by thermal energy or chemical reactions [1,3,4]. Lycopene, with its acyclic structure, large array of conjugated double bonds, and extreme hydrophobicity, exhibits many unique and distinct biologic properties. With the use of an in vitro system in which lycopene and some other carotenoids were bound to the surface of human lymphoid cells, it was recently demonstrated that lycopene provided the best protection against singlet oxygen-induced cell damage [1,4–6].

With the use of sophisticated food composition databases for epidemiologic studies, lycopene may increasingly be identified as sharing inverse relationships to cancer with other common carotenoids or as being the only carotenoid to show such an association. A rapidly accumulating and overwhelming amount of evidence from various epidemiologic studies around the world suggest that a diet containing tomatoes and tomato products results in a lower risk for several types of cancer [1,3,7-12].

Carotenoids, which are transported in the blood by lipoproteins, appear to concentrate in specific tissues that have a large number of low-density lipoprotein receptors and a high rate of lipoprotein uptake such as liver, adrenals, and testes [1]. As with other carotenoids, lycopene occurs in various geometrical isomers. cis isomers of lycopene make up more than 50% of the total lycopene in human serum and other tissues. This is in contrast to the food sources where they originate; in tomatoes and tomato-based products, all-trans lycopene comprises 79% to 91% of total lycopene. cis isomers of lycopene are more bioavailable than trans-lycopene, probably because the cis isomers are more soluble in bile acid micelles and may be preferentially incorporated into chylomicrons.
Heat processing increases the bioavailability of lycopene by breaking cell walls and allowing extraction of the lycopene from the chromoplasts, where it is found in raw tomatoes [15-17]. Tomatoes and related tomato products are the major source of lycopene. The amount of lycopene in fresh tomato fruits depends on the variety, maturity, and environmental conditions under which the fruit matured. More than 80% of processed tomatoes are consumed in the form of tomato juice, paste, puree, ketchup, sauce, and salsa [2,18].

In the present study, information about the lycopene content of tomatoes and tomato products used in the preparation of tomato-based foods and consumed by young populations of Croatia in the institutional food service was examined. The study evaluated the daily contribution of lycopene from these products in the diet of Croatians, which is one of the Mediterranean countries with dietary patterns that often includes tomato-based foods. This study raised important questions about the importance of lycopene in the diet and the difficulties in setting recommendations for optimal daily lycopene intake.

2. Methods and materials

2.1. Tomatoes and tomato products

Commercially available fresh tomato fruits grown in 3 different geographic regions of Croatia (24 different samples) and commercially available in tomato products (8 different products), including puree (15 brands), hot ketchup (8 brands), mild ketchup (9 brands), plain ketchup (11 brands), double concentrated paste (21 brand), triple concentrated paste (2 brands), tomato juice (6 brands), and whole canned tomatoes (10 brands), were purchased from local supermarkets in Zagreb, Croatia.

2.2. Chemicals and instrumentation

Lycopene standard and solvents (hexane, ethanol, and acetone) were obtained from Sigma Chemical Co (St. Louis, MO). A Hitachi U-2010 spectrophotometer Micro Scan 4GP/ADI (Hitachi, Ltd., Tokyo, Japan) was used for lycopene analysis. Homogenization of the samples of fresh tomatoes and whole canned tomatoes was done using a Moulinex Optiblend 2000 Duo (Moulinex, Lyon, France) blender.

2.3. Lycopene measurement

The samples of fresh tomato or tomato product were carefully weighed (4 F 0.01 g) into a 200-mL flask wrapped with aluminum foil to keep out light. The samples of fresh tomatoes and whole canned tomatoes were homogenized in a blender. A 100-mL mixture of hexane-acetone-ethanol, 2:1:1 (vol/vol%), was added to the flask and agitated continuously for 10 minutes on a magnetic stirrer plate, after that, 15 mL of water was added followed by another 5 minutes of agitation. The solution was separated into distinct polar and nonpolar layers [19]. The hexane solution containing lycopene was filtered into a 0.2-lm filter paper trough; the filtrate was then diluted with a mixture of hexane-acetone-ethanol (2:1:1, vol/vol%). The residue on the filter paper was colorless, indicating rapid and complete extraction of lycopene [19]. Lycopene concentration was estimated by measuring the absorbance of the hexane solution containing lycopene at 472 nm on a spectrophotometer. Each sample of fresh tomato and each brand of tomato product were extracted twice in triplicate analysis, yielding 12 results for each fresh tomato or each brand of tomato product.

The lycopene was quantified by use of a standard linear curve (R2 = 0.9996) of lycopene solution in hexane in concentrations from 0.25 to 1.25 lg/mL. The contents of lycopene were expressed as milligrams per 100 g wet weight. The results of determination of lycopene content in tomatoes and tomato products were analyzed statistically, using analysis of variance [20] and Duncan test [20].

2.4. Estimation of dietary intake of lycopene

Lycopene data from the analytical results were used for calculation of the intake of this compound. Tomato-based foods provided to groups of approximately 1000 nursery children (aged 2-6 years), 600 school children (aged 6-14 years), and 700 university students (aged 18-24 years) in the institutional food service (nursery, school and university cafeteria) were observed periodically during 6 months for the content of tomatoes and tomato products used during cooking. Using the analytical data, we calculated the lycopene content of these meals. Based on the data of lycopene content per serving of the meal, the daily cafeteria meal intake of lycopene (from tomatoes and tomato products) in nursery children, school children, and university students was estimated. Days without tomato-based foods at the cafeteria, weekends, days at home, or tomato-based foods at home were not taken into account.

3. Results and discussion

3.1. Lycopene content of commercially available tomatoes and tomato products

Lycopene content of fresh tomatoes and tomato products was determined by a spectrophotometric method after rapid extraction [19]. Sharma and Le Maguer [21] and Rao et al [22] demonstrated that
lycopene can be accurately estimated by using either high-performance liquid chromatography or spectrophotometric method. Lugasi et al. [23] also indicated that spectrophotometry is an acceptable method in the case of those foods in which lycopene is the predominant carotenoid. b-Carotene is present in tomatoes, but in small amounts, and the absorption maximum of b-carotene is different from that of lycopene [21]. Sharma and Le Maguer [21] found that a spectrophotometric method enabled them to accurately quantify lycopene. They found no significant difference in the amount of lycopene determined by using high-performance liquid chromatography and spectrophotometric method.

Fresh tomatoes grown in 3 different geographic regions of Croatia had significantly different lycopene content (P <0.05), which ranged from 1.82 to 11.19 mg per 100 g wet weight (Table 1). For the calculation of lycopene intake, an average value of 5.26 mg per 100 g wet weight was used. The literature reports that the lycopene content in fresh tomatoes varies depending on the variety, maturity, and environmental conditions under which the fruit matured [18]. Hart and Scott [24] reported that lycopene content in different varieties of tomatoes commonly consumed in the UK ranged from 1.58 to 5.65 mg per 100 g (red varieties).

A wide range of lycopene content was observed in different commercially available tomato products from markets in Zagreb, Croatia (Table 1). In the case of all kinds of tomato products, statistically significant differences in lycopene content were found between different brands within the same kind of tomato product (P <0.05). In the 15 analyzed brands of tomato puree (the best selling tomato product on Croatian markets), the values of lycopene content ranged from 5.56 to 16.94 mg per 100 g wet weight, with an average value of 10.21 F 3.20 mg per 100 g. Similar concentrations of lycopene in tomato products were reported in the literature [2,19,22-24]. In 3 of 28 brands of ketchup (hot, mild, and plain ketchup), the values of lycopene content were lower or higher than those found in literature, whereas other results were very similar to published data [2,22,23,25,26]. Double concentrated tomato paste of 21 different producers had variable lycopene levels ranging from 3.80 to 49.46 mg per 100 g wet weight, with an average value of 25.22 F 14.87 mg per 100 g. The results of analyses of lycopene content in the samples of triple concentrated tomato paste were very similar to the average value of lycopene content in the samples of double concentrated tomato paste. Generally, the lycopene content in some samples of double concentrated products was lower than expected, probably because of lycopene degradation during tomato processing. In this regard, lower concentrations of lycopene were found than reported by others in 8 brands of double concentrated tomato paste, whereas the results of lycopene content in triple concentrated tomato paste were in agreement with the literature [2,22,23,25,26].

The results of lycopene content in 3 different brands of tomato juice (6.93, 13.63, and 7.50 mg per 100 g) were similar to published values [22,23,26]. In another 3 analyzed brands of tomato juice, a much higher lycopene amount was found (21.42, 28.35, and 42.74 mg per 100 g). In a critical review, Shi and Le Maguer [2] reported that some authors reported high amounts of lycopene (61.60 mg per 100 g wet weight) in commercial samples of tomato juice. Only 3 of a total of 10 analyzed brands of whole canned tomatoes were in agreement with the literature [23-25].

After comparison of the average values of lycopene content in different tomato products, expressed as milligrams per 100 g wet weight, we can conclude that the highest average lycopene content in this study was in the group of concentrated tomato paste and the lowest in the group of plain ketchup. Statistical analysis of the results indicate that lycopene content in tomato puree, hot ketchup, mild ketchup, double concentrated paste, triple concentrated paste, tomato juice, and whole canned tomatoes was different between all kinds of tomato products (P < 0.05). This was expected because it is known that processing of tomato products involves different thermal and mechanical treatments that may affect tomato product quality and also the content of lycopene. The differences in lycopene content of tomato products are presented in Table 1.

### 3.2. Lycopene intake

Daily cafeteria meal lycopene intake (from tomatoes and tomato products) in 3 young population groups of Croatia was estimated on the basis of analytical results reported above, as well as
on the content of tomatoes and tomato products in tomato-based foods provided to nursery children aged 2 to 6 years (approximately 1000 children), school children aged 6 to 14 years (about 600 children), and university students aged 18 to 24 years (about 700 students) in a 6-month period. The effects of processing on the lycopene content of foods are conflicting. The stability of lycopene may be variable in different food systems because of the complex nature of food components, and their stability has not yet been rigorously addressed. The presence of fat, the change in percentage of solids, and the severity of heat treatment were not contributing factors in the formation of lycopene isomers in tomato products, except at extreme conditions not regularly used in the food industry or during food preparation [27-29]. Therefore, it was hypothesized that the lycopene content of tomatoes and tomato products was not decreased significantly after a heating time of 5 to 10 minutes during preparation of the tomato-based foods. Lycopene content (milligrams per serving) of the meals periodically offered to nursery children, school children, and university students during a 6-month period in cafeterias is shown in Tables 2-4. The estimated daily cafeteria meal intake of lycopene (from tomatoes and tomato products) in the nursery children group was 4.82 mg; in the school children group, 4.11 mg; and in the university student group, 3.35 mg. It is important to note that meals containing tomatoes and tomato products were not provided every day during the 6-month observation period, and lycopene intake was not accounted for the conditions previously stated (weekends and days at home).

The lycopene intake from cafeteria meals shows differences among the groups. In preparing the meals in nursery and school cafeterias, different kinds of tomato products were used and also fresh tomatoes in amounts that provide higher lycopene intakes to groups of nursery children and school children than those in the group of university students. The estimated lycopene intakes of young Croatian population groups are similar to those estimated in the Hungarian [23] population group of children (2.99 mg) and group of adults (4.26 mg), higher than the Dutch [30] (1.0-1.3 mg) and German [31] (1.28 mg), but lower than the American [32] (7.78 mg for all age groups). This is probably the result of similarities of the nutritional habits between Hungarian and Croatian populations and the differences in the nutritional habits between the Croatian population and the population from the other countries mentioned. In addition, the lycopene content in fresh tomatoes and tomato products as well as the amount of lycopene in tomato-based foods can vary.

Many authors have studied the dietary carotenoid intakes of subjects, but there are no data on the optimal levels [33]. A large body of epidemiologic data suggests that higher blood concentrations of carotenoids obtained from foods are associated with a lower risk of several chronic diseases. This evidence, although consistent, cannot be used to establish a requirement for carotenoid intake because the observed effects may be due to other substances found in carotenoid-rich food, or to other behavioral correlates of increased fruit and vegetable consumption. Although no dietary reference intakes are proposed for carotenoids at present, existing recommendations for increased consumption of carotenoid-rich fruits and vegetables are supported [34]. Rao and Shen [35] studied the effect of low-dose lycopene intake on lycopene bioavailability and oxidative stress. Based on their
results, these authors recommended a daily intake of lycopene of 5 to 10 mg. Tomato-based meals in nursery, school, and university cafeterias in Croatia provide a slightly lower lycopene intake from this recommendation. More studies should be undertaken to establish the daily lycopene intake for different Croatian population groups to insure health and well-being.

In conclusion, this study showed that nutritional habits in Croatia, one of the Mediterranean countries, which often includes tomato-based foods consumption, can provide at least 3 mg of lycopene a day. In addition, this study showed the importance of new investigations in this field of nutrition to establish recommendations for optimal daily lycopene intake.

Acknowledgment

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References

1. 6 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
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+, Mg2+, Ca2+ 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 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 C18 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 cm³.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 cm³ 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 D65 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⁻¹ L-histidine monohydrochloride, 0.1% MHEC, 6 mmol.dm⁻¹ histidine + 2 mmol.dm⁻¹ CaCl₂, 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 cm³ of concentrated HNO₃ was added and mixed. The mixture was placed in a warm sand bath (temperature approximately 250 °C) and evaporated until the mixture was 1 cm³. After dropping temperature, 3 cm³ of concentrated HClO₄ was added and the mixture was heated again. When intensive white smoke appeared, the mixture was taken from sand bath. After smoking, 0.6 cm³ of concentrated H₂O₂ was added and the sample was quantitatively poured into 50 cm³ of volumetric flask.

<table>
<thead>
<tr>
<th>The instrumental parameters</th>
<th>K</th>
<th>Mg*</th>
<th>Ca*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength [nm]</td>
<td>766.5</td>
<td>285.2</td>
<td>422.7</td>
</tr>
<tr>
<td>Supply current of HCL lamp [mA]</td>
<td>12</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>Gap [nm]</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Air flow [dm³.min⁻¹]</td>
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<td>2.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Acetylene flow [dm³.min⁻¹]</td>
<td>8.0</td>
<td>8.0</td>
<td>8.0</td>
</tr>
</tbody>
</table>

1 Mg and Ca were measured with addition of elimination solution containing 1 g dm⁻³ La and 5 g dm⁻³ of β-hydroxycholinolink

**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 (Commission Regulation (EEC) No 1764/89 1986). The pH values were ranged between 3.6 and 4.3, so all samples fulfilled this requirement.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Soluble solids [%]</th>
<th>pH</th>
<th>HMF [mg.kg(^{-1})]</th>
<th>(a^<em>/b^</em>)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 K</td>
<td>25.0</td>
<td>4.2</td>
<td>nd</td>
<td>2.1</td>
</tr>
<tr>
<td>2 K</td>
<td>24.0</td>
<td>4.2</td>
<td>nd</td>
<td>2.0</td>
</tr>
<tr>
<td>3 K</td>
<td>25.0</td>
<td>4.2</td>
<td>nd</td>
<td>2.0</td>
</tr>
<tr>
<td>4 K</td>
<td>25.0</td>
<td>4.3</td>
<td>nd</td>
<td>2.0</td>
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<tr>
<td>5 K</td>
<td>25.1</td>
<td>4.3</td>
<td>nd</td>
<td>1.9</td>
</tr>
<tr>
<td>6 K</td>
<td>24.5</td>
<td>4.2</td>
<td>nd</td>
<td>2.0</td>
</tr>
<tr>
<td>7 K</td>
<td>25.1</td>
<td>4.3</td>
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<td>4.1</td>
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<td>2.0</td>
</tr>
<tr>
<td>9 K</td>
<td>24.5</td>
<td>4.2</td>
<td>nd</td>
<td>2.1</td>
</tr>
<tr>
<td>10 K</td>
<td>24.6</td>
<td>4.2</td>
<td>nd</td>
<td>2.1</td>
</tr>
<tr>
<td>11 K</td>
<td>24.6</td>
<td>4.2</td>
<td>nd</td>
<td>2.0</td>
</tr>
<tr>
<td>K 6.0</td>
<td>25.0</td>
<td>4.3</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>K 6.5</td>
<td>25.5</td>
<td>4.3</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>K 7.5</td>
<td>25.1</td>
<td>4.3</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>K 8.0</td>
<td>25.5</td>
<td>4.3</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>AK</td>
<td>25.9</td>
<td>4.1</td>
<td>22.44</td>
<td>1.6</td>
</tr>
<tr>
<td>BK</td>
<td>25.5</td>
<td>4.3</td>
<td>16.53</td>
<td>2.0</td>
</tr>
<tr>
<td>CK</td>
<td>27.8</td>
<td>3.9</td>
<td>2.98</td>
<td>2.0</td>
</tr>
<tr>
<td>DK</td>
<td>23.4</td>
<td>4.0</td>
<td>18.24</td>
<td>1.7</td>
</tr>
<tr>
<td>EK</td>
<td>32.7</td>
<td>3.9</td>
<td>2.95</td>
<td>1.6</td>
</tr>
<tr>
<td>FK</td>
<td>14.6</td>
<td>3.6</td>
<td>7.83</td>
<td>1.6</td>
</tr>
<tr>
<td>GK</td>
<td>28.2</td>
<td>4.1</td>
<td>28.40</td>
<td>2.2</td>
</tr>
<tr>
<td>HK</td>
<td>27.3</td>
<td>3.9</td>
<td>7.90</td>
<td>1.8</td>
</tr>
<tr>
<td>IK</td>
<td>28.2</td>
<td>3.8</td>
<td>4.33</td>
<td>1.8</td>
</tr>
<tr>
<td>JK</td>
<td>26.5</td>
<td>4.1</td>
<td>nd</td>
<td>2.1</td>
</tr>
</tbody>
</table>

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>
<thead>
<tr>
<th>Sample</th>
<th>Formol number [cm$^3$ 0.1 M NaOH/100 g]</th>
<th>Citric acid [mg/100g]</th>
<th>Malic acid [mg/100g]</th>
<th>PCA [mg/100g]</th>
<th>K$^+$ [mg/100g]</th>
<th>Mg$^{2+}$ [mg/100g]</th>
<th>Ca$^{2+}$ [mg/100g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 K</td>
<td>40.7</td>
<td>527.6</td>
<td>64.9</td>
<td>258.3</td>
<td>354.9</td>
<td>14.6</td>
<td>18.5</td>
</tr>
<tr>
<td>2 K</td>
<td>38.4</td>
<td>576.3</td>
<td>70.5</td>
<td>190.3</td>
<td>327.2</td>
<td>13.6</td>
<td>17.6</td>
</tr>
<tr>
<td>3 K</td>
<td>43.6</td>
<td>559.2</td>
<td>67.4</td>
<td>143.8</td>
<td>367.8</td>
<td>14.3</td>
<td>18.3</td>
</tr>
<tr>
<td>4 K</td>
<td>38.7</td>
<td>498.4</td>
<td>54.0</td>
<td>182.7</td>
<td>306.1</td>
<td>14.7</td>
<td>21.8</td>
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<tr>
<td>5 K</td>
<td>50.7</td>
<td>587.6</td>
<td>67.5</td>
<td>159.4</td>
<td>331.8</td>
<td>15.2</td>
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<tr>
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<td>643.1</td>
<td>72.9</td>
<td>237.8</td>
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<td>20.5</td>
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<td>50.5</td>
<td>503.5</td>
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<td>303.4</td>
<td>15.7</td>
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<tr>
<td>8 K</td>
<td>39.0</td>
<td>601.0</td>
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<td>211.8</td>
<td>332.6</td>
<td>13.9</td>
<td>17.8</td>
</tr>
<tr>
<td>9 K</td>
<td>44.1</td>
<td>708.2</td>
<td>56.4</td>
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<td>11 K</td>
<td>43.1</td>
<td>588.9</td>
<td>58.4</td>
<td>181.8</td>
<td>365.0</td>
<td>14.7</td>
<td>18.5</td>
</tr>
<tr>
<td>K 6.0</td>
<td>31.2</td>
<td>574.6</td>
<td>74.1</td>
<td>190.3</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>K 6.5</td>
<td>36.4</td>
<td>558.0</td>
<td>61.6</td>
<td>198.5</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>K 7.5</td>
<td>37.3</td>
<td>639.3</td>
<td>70.3</td>
<td>217.1</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>K 8.0</td>
<td>64.9</td>
<td>673.3</td>
<td>77.4</td>
<td>228.3</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
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.
References

1. 7 Dehydrated Tomatoes

I. INTRODUCTION

Tomato (*Lycopersicum esculentum*) is a true fruit, but is usually regarded and consumed as a vegetable with savory dishes. It is Australia’s second largest commercial vegetable crop, with a harvest of 414,000 metric tons in 1999–2000. Victoria is the main growing state, accounting for 60% of the national harvest. The tomato is also the world’s most widely grown vegetable after the potato. World tomato production in 2000 was estimated at almost 100 million metric tons, an increase of 31% over the last decade. Almost half of this increase is attributable to China alone. Figure 1 shows the top ten tomato producing countries in the world with China as the largest producer followed by the United States.

![Figure 1: The top ten tomato production countries in the world. (From FAO, 2000.)](image)

In order to preserve fruit or vegetables that have been detached from the host material, food technologists must know how to minimize further chemical and in particular microbiological changes from taking place. All the different methods of food preservation have one thing in common: the aim is to stop or slow chemical reactions and microbial growth. Drying is a preservation method that reduces both chemical and microbiological changes by removing the water component in food.

Dehydrated tomato products fall into three main categories: tomato paste and its derivatives, tomato powder, and dehydrated tomato. Tomato paste is usually considered as semifinished product because it is commonly used as an ingredient in other food products such as pizza. In addition, tomato paste is commonly used as a raw material for products like tomato sauce and tomato powder. Fully dehydrated tomatoes are usually rehydrated before use or simply added to recipes that include water and allowed to soften. Semidried tomatoes are gaining in popularity as a gourmet semiprocessed vegetable in many parts of Australia and overseas. They are used mainly as ingredients in salads, spaghetti dishes, and homemade pizzas, or they are simply sold as marinated “roasted tomatoes” in delicatessens. Dehydrated tomatoes are prepared from fresh tomatoes. They are dried to varying moisture contents from about 35% (wet basis) for semidried to about 10% for fully dried using a range of dryers. They are usually packed in canola oil with added garlic, herbs, and spices. Other forms of using dehydrated tomato include tomato spread, tomato salsa, and tomato pesto. The headspace is usually flushed with nitrogen in order to extend the shelf life of the product.
II. NUTRITIVE VALUE

A. Importance of Lycopene in the Human Diet

The tomato is made up of skin, pericarp (wall), and locule (jellylike parenchyma cells), which surrounds the seed and normally contains between 4.5 to 8.1% total solids and 91.9 to 95.5% water content. Table 1 gives an overall picture of the nutritive value of the tomato, based on data from the USDA Nutrient Database, 2001. The tomato is generally considered a healthy food, as it is low in fat, free of cholesterol, and rich in vitamin A, vitamin C, and potassium. It is also a good source of fiber and protein. In addition, the tomato and tomato products are the major source of lycopene, an important contributor of carotenoid to the human diet. Lycopene is a natural pigment that gives the tomato and tomato products their characteristic red color and represents about 83% of the total pigments present. Most of the lycopene is found in the fiber portion of the tomato. Researchers found that the concentration of lycopene in tomato skin is about 3 to 5 times higher than in the flesh of a tomato. Lycopene is a member of the carotenoid family and appears to possess unique nutritional properties. Extensive research in this field has revealed that lycopene may provide protection against prostate cancer, lung cancer, and a range of epithelial cancers. It is an excellent singlet oxygen quencher, almost twice as good as beta carotene. It also has other good antioxidative properties.

According to work done by Boileau et al., the total lycopene content in tomato alone does not determine its nutritional and health benefits; rather, these properties are dependent to a large extent on the distribution of lycopene isomers. These researchers found that the cis isomers are more bioavailable than the trans form. This is in agreement with earlier work done by Britton and by Stahl and Sies. This work suggests that cis isomers of lycopene might be better absorbed than their all trans parent structure. It is generally accepted that fresh tomato contains over 95% of the all trans isomers, and processing the tomato causes lycopene to undergo isomerization: the amount of cis isomers increases as a function of temperature and processing time. The type of processing, such as dehydration method, is also important and will be discussed later.
B. Factors Affecting Lycopene Content

The amount of lycopene in fresh tomato fruit normally ranges between 3 and 5 mg lycopene per 100 g of raw material. This quantity is dependent on a number of factors including variety, season, and maturity of the tomatoes. Storage also affects the lycopene content. For example, tomatoes picked green and allowed to ripen in storage have a substantially lower lycopene content than vine-ripened tomatoes. In addition, Lurie et al. reported that high temperature (38°C) inhibits lycopene production, while low temperature inhibits both fruit ripening and lycopene production.

C. Stability of Lycopene During Processing

Several researchers have studied the effects of different cooking methods on the levels of lycopene. Shi and Le Mague showed the effect of dehydration methods (osmotic treatment, vacuum drying, conventional air-drying) on lycopene degradation and isomerization (Table 2). Conventional air-drying was found to bring about the highest lycopene loss, and the work showed a significant increase in cis isomers with a simultaneous decrease in the all trans isomers. In addition, Khachik et al. studied the effect of food preparation on qualitative and quantitative distribution of major carotenoid constituents of tomatoes and several green vegetables. These researchers show that cooking and various food preparation techniques affect the levels of carotenoids in vegetables, but lycopene in stewed tomato and tomato paste were found to survive the heat treatment. The qualitative distribution of lycopene in tomato paste remains identical to that of raw and stewed tomatoes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total lycopene (µg/g dry basis)</th>
<th>Lycopene loss (%)</th>
<th>All trans isomers (%)</th>
<th>Cis isomers (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh tomato</td>
<td>755ᵃ</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Osmotic treatment</td>
<td>755ᵃ</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Osmotic-vacuum dried</td>
<td>737ᵇ</td>
<td>2.4</td>
<td>93.5</td>
<td>6.5</td>
</tr>
<tr>
<td>Vacuum dried</td>
<td>731ᶜ</td>
<td>3.2</td>
<td>89.9</td>
<td>10.1</td>
</tr>
<tr>
<td>Air-dried</td>
<td>726ᵈ</td>
<td>3.9</td>
<td>84.4</td>
<td>16.6</td>
</tr>
</tbody>
</table>

Note: Data presented as means of triplicate determinations. Means in a column not sharing common superscript (ᵃ–ᵈ) are significantly different (p < 0.01).

D. Stability of Lycopene During Storage

The most important factors contributing to the degradation of lycopene are temperature, light, and the availability of oxygen during storage. Work done by Lovric et al. showed that lycopene in processed tomato products such as tomato powder is influenced by storage atmosphere and temperature (Fig. 2). They found that the percent retention of lycopene decreased at high temperatures and in the presence of oxygen.

Anguelova and Warthesen studied lycopene stability in tomato powders and concluded that lycopene degradation during storage of two types of tomato powder (hot-break and coldbreak) proceeded to the same extent with oxidation as the predominant mechanism of all trans lycopene loss. Exposure to air and increased temperature (up to 45°C) was found to have the most unfavorable effect on lycopene stability with an increase in autoxidation of lycopene.
while light and increased temperature appeared to be unimportant factors for the stability of lycopene in tomato powders during storage.

There is an emerging market for semidried tomatoes, and this product is found to have adequate shelf life with minimum oxidative heat damage (35). In addition, Zanoni et al. found that lycopene appears stable during drying and there is no loss of lycopene content during drying at 80°C, even though it is well known that lycopene is usually stable up to 60–65°C. However, they found that both the storage temperature and exposure to air and light affects the lycopene content of air-dried tomato halves.

![Figure 2](image)

**Figure 2** Total lycopene retention in tomato powder stored in different atmospheres, temperatures, and time periods. (From Lovric et al., 1970.)

### III. MICROBIOLOGY

Contamination of tomatoes can occur at various points during their journey from harvest to the processing plant, and identification of the likely source of contamination is important. Several outbreaks of human gastroenteritis have been linked to the consumption of contaminated tomatoes associated with pathogens such as *Salmonella javiana* and *Listeria monocytogenes*. In addition, botulism food poisoning has been associated with tomatoes contaminated with mold.

The tomato fruit contains 90–95% moisture content and is capable of supporting bacterial growth. According to Gould, the pH of tomato varies considerably, depending on important factors such as cultivar, maturity, and seasonal variation. However, the tomato is not considered a high-risk food, as the pH of the fruit generally ranges from pH 4.2 to 4.9 with an average of about 4.5. At this pH, most pathogens are unlikely to grow. However, the growth-limiting pH for *salmonella* was demonstrated to depend on the acid molecule itself in the test media. Wei et al. found that low pH values (4.2–4.4) in wounded red tomato flesh did not inhibit bacterial growth and attributed this observation to the acid molecule in tomato.
Draughon et al. found that *C. botulinum* is capable of growing in fresh tomato inoculated with mold. They suggested that the presence of molds probably causes the destruction of acid, and the pH of tomato-slices above the minimum required for growth and toxin production of *C. botulinum*. This finding is in agreement with work done by Robinson et al. where it was demonstrated that Clostridium only grew when mold was present.

Mold contamination is an important indicator of low-quality raw product in the tomato processing industry. According to Battilani et al., the species most frequently associated with spoiled tomatoes are *Alternaria alternata*, *Botrytis cinerea*, *Fusarium oxysporum*, *Geotrichum candidum*, *Phoma lycopersici*, *Rhizoctonia solani*, and *Rhizopus nigricans*. Yeong et al. studied the effect of storage temperature on keeping quality of tomato and concluded that storing it from 0 to 10°C is the best way to minimize mold growth, as mold infection is found to occur only at 15, 20, and 25°C.

**IV. PROCESSING**

**A. Preparation**

1. **Raw Material**

   Figure 3 shows an overview of the processing of dehydrated tomato and tomato products. High-quality attributes of fresh tomatoes are critical in order to obtain high-quality tomato end products. According to Goose and Binsted, a variety suitable for tomato paste manufacture should have a high soluble solids content, an intense red color, a good flavor, low acidity, and a reasonable amount of pulp. Before tomatoes are transported to the factory, they are graded according to grade standards. Grade standards will vary from country to country and may be used to determine the price to be paid per kilogram of tomato. For example, standards based on the FDA put fresh tomatoes into different grades, sizes, and maturity classifications based on color, size measurements, and defects such as mold, blemishes, and mechanical damage. Grade A is considered the best. Off-grade are those that fail to meet requirements. Tomatoes may also be classified according to total soluble solids (8Brix) with a specified minimum acceptable level. The average total soluble solids for tomato processing is about 4.78Brix and rarely goes below 4.08Brix or above 5.28Brix. At the factory, incoming loads of tomatoes are carefully checked for uniformity of color, size, maturity, mold growths, insect infestations and the presence of foreign matter.

   Fresh tomato used for manufacturing into dehydrated tomato halves or wedges needs to be consistent in size, free from blemishes, red in color but not too ripe, firm with thick-walled flesh, and most importantly free from mold and bacteria rot. The most important parameters indicating tomato quality appear to be color and firmness.
2. Washing

Water supplied to the factory for washing tomatoes must be clean, potable, and uncontaminated. Its essential role is to remove contaminants and reduce the initial microbial load on the tomato, although water is also used to cushion the unloading of tomatoes into the holding tank or soaking vat. According to Lund, proper washing of tomatoes at this stage can reduce the microbial load by a factor of 10–100, but it may not remove pathogens from the product surface. Washing methods vary from factory to factory and may be as simple as soaking the tomato in a static tank. The tank is regularly changed and maintained at up to 200ppm of available chlorine. More complex modern devices employ high-pressure water jets and agitation within the tanks by compressed air. However, the most commonly used method to control microbial populations in water for washing tomatoes is the addition of hypochlorite.
in the form of available chlorine, which produces hypochlorous acid at concentrations ranging from 10 to 200ppm. According to Dychdala, concentrations as low as 0.5–10ppm are sufficient to kill the suspended vegetative cells of bacteria. Both Dychdala and Robbs et al. found that higher concentrations are required to kill bacterial or fungal spores. Recommendations for water chlorination in tomato processing plants usually range from 100–300ppm (well above the minimum lethal dose for spores) because chlorine is highly unstable in solution and is easily inactivated by the presence of soil.

3. Sorting and Trimming

Methods of sorting and trimming vary. Sorting and trimming are usually done on a roller conveyor where the tomatoes are rotated to allow sorters full view of the raw material. This task requires skill in differentiating between tomatoes that must be rejected and those that only require trimming to remove partly defective parts. The defective tomatoes are removed manually. Goose and Binsted give a summary of defects such as ground rot and sunscald found in tomatoes during sorting, and this summary is a useful guide during the sorting and trimming stage. The extent or strictness of sorting depends on the quality of end product desired.

B. Fresh Tomato to Dehydrated Tomato

1. Cutting
After sorting and grading, the tomatoes are washed in chlorinated water (50–200ppm), rinsed, and transported to the cutting machine prior to the drying process.

2. Drying

   a. Background Over the decades, the technology for the dehydration of foods has improved tremendously. A great variety of sophisticated drying techniques have been developed to retain product quality and improve energy efficiency. In the late 1970s, freeze-drying was considered the most promising method of drying foods because of its superior end product quality, which was lacking in air-drying. However, freeze-drying is an expensive process and may not be economically viable for drying low-value products. Over the last decade, the heat-pump dryer is emerging as a promising alternative to the conventional hot-air dryer.

   b. Hot-Air Drying Conventional drying using preheated air is by far the dominant and most economical system used in the food industry. In conventional dryers, preheated air (usually at 60°C to 110°C, air velocity of 0.5 to 2m/s and varying relative humidity depending on the weather) is blown across the product surface. Water extracted from the product is then carried away by the air moving out of the chamber as water vapor. As the air becomes depleted in the chamber, more ambient air is drawn into the drying chamber and reheated. Drying times are usually very long (10 to 20 hours) and depend on the load. These long drying processes at high temperature in the presence of oxygen are typical conditions for oxidative heat damage of the product. The low efficiency of conventional dryers is due to the loss of latent heat of water vapor and the heating of the replacement air. Other limitations of hot-air drying include the dependency of the drying rate on the thermal conductivity of the material, and the overheating of the surface, which causes case hardening. This leads to an inferior product quality and a poor drying rate.
c. Heat-Pump Dehumidifier System The major differences between the heat-pump dryer and the conventional hot-air dryer are that the relative humidity (typically 8 to 15%) can be controlled in heat pump system; also the heat pump dryer removes water from products without ventilation, and the system is totally recirculatory. In the heat-pump dehumidifier system, warm dry air (typically 50 to 55°C) is taken off the condenser and pumped through a drying chamber containing the wet product. As moisture is removed from the product, the air is cooled and becomes more humid. The cool, humid air moves over the evaporator, which causes condensation. The same air is then pumped back over the condenser to heat it again—completing the cycle. As the system is totally enclosed, there is the possibility that microbes from raw material could be distributed throughout the dryer via the evaporator and condenser coils. The key features of the heat-pump dryer system are shorter drying times and lower drying temperatures, resulting in less oxidative heat damage of the product.

d. Microwave Drying Microwave drying may produce better quality dehydrated products while considerably reducing the drying duration. However, it is well known that microwave heating results in uneven cooking.

To make drying successful with microwaves alone, it is necessary to dry the tomato at such a rate that its interior never reaches the critical temperature at which the product deteriorates. This requires a sophisticated feedback control system. In addition, water that has been evaporated must not be allowed to condense in the drying chamber. This tends to occur when there is no airflow to carry the vapor away. One of the key advantages of microwave drying is the rapid heating and drying. Energy extracted from the electric field is preferentially absorbed by the water molecules at the points where the water resides in the product. This eliminates the need for the heat to be conducted in from the surface of the product, as is the case in conventional dryers.

e. Combined Systems The use of microwave energy alone for drying is not feasible, as the evaporated moisture must be carried away from the product and the drying chamber, otherwise the condensate will be reabsorbed by the microwave energy. The combination of microwaves and hot air offers a practical solution, as the hot air not only imparts energy to the product but also carries the evaporated moisture away.

Attempts have been made by several researchers to combine microwaves and hot air. Bhartia et al. performed preliminary studies on the optimization of temperature, air velocity, and microwave power level on the drying of material with varying hygroscopicity. The results indicate that the combined process reduces the total energy required to about one-third when compared with hot air only. Smith reviewed dryers that use a microwave–hot air system for the drying of pasta, onions, and bacon and found that work done on macaroni achieves a quality that is superior for both cooked and uncooked pasta in terms of enhanced color, better “bite,” and reduced infestation. There was also a reduction of the bacteria count (by 90%) in the finished product. The combined system has advantages such as less shrinkage, increased rehydration capacity, and increased drying rate. A further advantage of combining microwave and conventional heating methods is the more uniform heating of foods and destruction of bacteria.
C. Fresh Tomato to Tomato Paste

1. Crushing or Breaking

After a final wash and spray using water jets, the sorted and trimmed tomatoes are quickly preheated before chopping=crushing to form the pulp. Alternatively, the tomatoes are chopped at room temperature and immediately, or within seconds of crushing, heated to a temperature range of 60 to 90°C (depending on the type of desired final product specification). This type of treatment is known as hot break treatment.

Rapid heating is essential to destroy enzymes and prevent the breakdown of pectin in tomatoes for some tomato products such as paste. It also liberates the locules that surround the tomato seeds and contribute to the overall texture or body of the finished product. As soon as the tomato is crushed, enzymes are released that could lead to the breakdown of pectin. Pectin occurs naturally in ripe tomatoes. Both pectin and protopectin are the major components found mainly between adjacent microscopic cells known as the middle lamella, which serves to cement the cells together and is partly responsible for the firm texture of the fresh tomato. However, as tomato ripens, the firmness of the tomato is reduced. This could be explained by the breakdown of protopectin into pectin, while the pectin in the cell walls is degraded into soluble compounds that have little binding power. The presence of pectin contributes to the viscosity of the final product. To prevent pectin breakdown, enzymes released from the crushing or chopping of tomatoes need to be destroyed as quickly as possible. According to McColloch and Kertesz and Foda and McCollum, the enzymes involved are pectinesterase, polygalacturonase, and cellulase. These enzymes are promptly inactivated when the tomatoes are heated rapidly above 82°C.

In cold-break treatment, the tomatoes are crushed at room temperature. In some tomato products such as soup, where “thickness” is not the sought-after quality, attention is usually focused on the color and flavor. These products are processed using lower break temperatures of between 60 and 65°C. Sherkat and Luh demonstrated that pectic retention and consistency of tomato pastes are influenced by the break temperature, where pectin retention decreases as the break temperature is lowered from 104 to 70°C.

2. Extraction and Juice Refining

To refine the juice, broken and preheated tomato pulps are screened by pumping to a series of extractors or cyclones using an initial screen with a sieve diameter of about 1mm followed by a second screen with a sieve diameter of between 0.4 and 0.7mm. These screens are designed to remove the seed, the skin, and any other pulp. This waste stream contains a high proportion of lycopene and can be an important source of lycopene for the food industry (5,59). In addition, the seed, which is a major part of the solid waste, can be utilized as a source of oil. A yield of 3% skins and seeds and 97% juice is considered high extraction. However, it may be commercially more feasible to extract only 70–80% juice and leave the residues for use in other tomato products. According to Leonard, a low extraction yield at 70% is desirable, since the extracted juice will be of improved quality by containing a higher percentage of soluble solids and a lower percentage of insoluble solids. Once the juice is refined, it is ready to be concentrated.
3. Concentrating

The concentrating stage (by evaporation of water) results in progressive increase in solids content of the pulp until a paste of the desired concentration and viscosity is reached (usually approximately 30% solids content). The method by which the juice is concentrated varies from tanks with coils in batch-type vacuum evaporators to continuous vacuum evaporators with a series of effects such as single effect to quadruple effect. The tomato soluble solids (TSS) define the range of tomato products. For example, according to the FDA’s standard of identity, tomato paste must contain not less than 24% TSS while tomato puree or pulp must contain not less than 8% TSS but less than 24% TSS.

4. Sterilization and Packaging

After concentration, the tomato paste is held in a closed tank and is canned conventionally or aseptically packaged. Canned tomato paste is usually hot-filled at a minimum temperature of 90°C into cans of varying size depending on the end use. It is then sealed without further heat treatment and passed through a water spray to remove any residue on the outside, cooled, and packed. Aseptic packaging of tomato paste usually involves heat treatment at a temperature of 105 to 110°C, cooling to 35 to 38°C, and filling aseptically into high-barrier aseptic bags.

5. Finished Product Evaluation

The best quality tomato paste is that which consistently meets the specifications of the customer or end user. The FDA’s standard of quality for tomato concentrates specifies (a) the strength and redness of color of the concentrate, (b) the number of whole seeds per 600g of concentrate, (c) the number of defects such as pieces of peel, seeds, or black particles per 100g of the product. In addition, routine laboratory analysis is usually used as a measure of quality and consistency for the customers. These include (a) natural total soluble solids—°Brix expressed as percentage of sucrose, (b) consistency—Bostwick consistometer [12.5 dilution, 30 seconds, expressed in cm], (c) serum separation—blotter test, for hot break only, expressed in mm, (d) the total acidity and pH—significant variations between varieties (3) but usually aimed at a final pH of about 4.3 in the tomato paste, and (e) the mold count—the presence of large numbers of mold usually indicates the use of moldy raw material and poor sorting and trimming.

D. Tomato Paste to Tomato Powder

1. Overview

Further concentration of tomato solids from 30–40% in tomato paste to about 97% results in tomato powder. The raw material used for tomato powder is tomato paste that is usually prepared by the hot break method. According to Masters, powder produced from cold break paste tends to have fewer desirable characteristics on reconstitution, as the solids generally settle after approximately 60 seconds rather than remain in homogeneous suspension. As tomato powder is usually not produced from a seasonal raw material, production can occur throughout the year.
2. Drying

Tomato powder is usually manufactured from roller-drum-dried, foam-mat-dried, or spray-dried material. Of all the drying techniques tried, spray-drying appears to be the most suitable to produce high-quality powder economically. Owing to the thermoplastic nature of tomato powder, the drying chamber needs to be designed to enable droplet drying to proceed without overheating. In addition, the system needs to be designed to handle the hygroscopic nature of the finished product from the drying chamber to the packing stage without contact with the surrounding air.

The traditional types of spray-dryer designs tend to suffer from deposit losses, product quality degradation, and frequent cleaning procedures. More recently, a high-capacity spray-dryer designed especially to overcome the shortcomings of the traditional spray-dryers was introduced. The drying chamber consists of a cocurrent nozzle tower dryer with a built-in conveyor belt, into which atomized paste and drying hot air are introduced from the ceiling. Figure 4 shows a schematic diagram of a filtermat dryer. The main drying chamber 1, with an airflow pattern, directs the particles downwards onto the moving belt, which forms the first stage of drying. The second stage takes place as the semidried particles are conveyed through drying chambers 2 and 3. The ability to control the air temperatures in these chambers allows much control and flexibility regarding the finished product specification. The tomato powder is cooled and conditioned in the last chamber 4, where it is usual to use dehumidified, cooled air, after which the powder falls off the belt and is sieved prior to being packed or conveyed into silo storage.

3. Finished Product Evaluation

Two of the most important factors affecting the shelf life of the finished product are the exclusion of oxygen and the temperature of storage of the packaged powder. Vacuum packaging and hermetic seals are important in maintaining the required shelf life in tomato powder. Other quality tests usually carried on the powder are moisture content, color, dispersibility, and ease of reconstitution.
Figure 4 A schematic diagram of a Filtermat Dryer. (Courtesy of Niro.)

References:
1. 8 Quality and authenticity control of fruit pure’es, fruit preparations and jams—a review

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Adulteration of foods is a serious economic problem concerning most food commodities, in particular fruit products. Since high-priced fruits command premium prices, producers of fruit-based products such as juices, jams, jellies, pure’es, and fruit preparations might be tempted to blend these products with cheaper fruits. In addition to admixtures of adulterants, the labelled fruit contents may not be met. Both types of adulteration are difficult to detect and lead to a deterioration of product quality. For consumer protection and to avoid unfair competition, it is of essential importance to guarantee both authenticity and compliance with the product specification. While approaches for the detection of fraudulent admixtures to fruit juices have extensively been reviewed, the objective of the present treatise is to provide an overview of the approaches so far suggested to detect and even quantify adulterations of the above-mentioned fruit products.

Introduction

Fruit preparations represent intermediate products used in fermented milk products such as yogurt, sour milk and fresh cheese, and in pudding, cream, fruit milk and ice cream. Another application is their use in bakery products and confectionery. According to the German Association for Food Law and Food Science (BLL) definition, fruit preparations are products meant for the production of dairy products which, as a rule, are produced from fruits or fruit constituents and various sugars, and also essences, flavours, colouring foodstuffs, thickening agents and consumable acids, and which are preserved by appropriate methods. The BLL guideline also specifies the quality requirements for fruits and fruit constituents meant for processing (Carle, 1997). Accordingly, the fruits should be healthy and fresh, unfermented, and have a ripeness degree appropriate for processing. Fresh fruit or fruit concentrate as well as concentrated fruit constituents may be used. The fruit content of the fruit preparations generally amounts to 35%. However, in the case of raspberry, raspberry-blackberry, redcurrant, gooseberry, plum and pineapple, the fruit content is at least 30%, and for banana and blackcurrant at least 25%. Colouring foodstuffs such as juices from cherry, grape or red beet, are not considered part of the fruit content. Depending on the intended use, the dosage of fruit preparations in dairy products ranges between 5 and 25%. The minimal amount of fresh fruit in yogurts with fruits is usually 6%. In the case of flavour-intensive fruits only 2% fruit is sufficient. Due to the low fruit contents and the complex matrix, quantitative and even qualitative analysis of fruit constituents in the end product is a very demanding challenge.

In contrast to fruit preparations, jams are usually destined for sale to the end consumer. The EU Council Directive 2001/113/EC of 20 December, 2001, relating to jams, jellies and marmalades and sweet chestnut pure’e intended for human consumption specifies both definitions and labeling of jams and related products. According to this directive, jam is a mixture, brought to a suitable gelled consistency, of sugars, the pulp and/or pure’e of one or more kinds of fruit and water. The quantity of pulp and/or pure’e used for the manufacture of 1000 g of finished product shall not be less than 350 g as a general rule, 250 g for redcurrants, rowan berries, sea-buckthorns, rosehips and quinces, 150 g for ginger, 160 g for cashew apples, and 60 g for passion fruit. In the case of ‘Extra jam’, the quantity of pulp used shall not be less than 450 g per 1000 g of the finished product. All products defined in part I of Directive 2001/113/EC must have a soluble dry matter content of 60% or more as determined by refractometer, except for those products where sugars have been entirely or partially replaced by sweeteners.

It is self-evident that the fruit content represents the main quality parameter of fruit pure’es, fruit preparations and jams. From a regulatory point of view, the specifications and the labelled composition of fruit-based products have to be met in order to maintain product quality and authenticity. From an economic point of view, product quality is also major issue of competition between producers. In addition, quality and authenticity are of particular importance with respect to consumer expectation. Fruit pure’es, fruit preparations and jams command premium prices and therefore represent favoured targets for adulterations, e.g. by blending high-priced fruits with cheaper fruits. In addition to admixture of adulterants, the specified fruit contents may not be met.

For this reason, numerous attempts at finding suitable methods for authenticity control and determination of the fruit content in fruit based
products have been made. The major analytical problem is due to the complexity of the products and to the substantial variance of the fruit specific components. Analytical techniques to face this challenge are at least as manifold as are the ways of adulteration, ranging from classical determination of chemical parameters to highly sophisticated instrumental techniques. While related reviews published during the past years focussed on foods in general (Cordella, Moussa, Martel, Shirrazouli, & Lizzanti-Cuvelier, 2002), on special techniques such as DNA-based and biotechnological methods (Lees, 2003; Lockley & Bardsley, 2000; Popping, 2002; Tzouros & Arvanitoyannis, 2001) or on different food groups (Arvanitoyannis & van Houwelingen-Koukaliaroglou, 2003; Bogdanov & Martin, 2002; Martinez et al., 2003), the objective of the present treatise is to summarise studies so far conducted on authenticity and quality control of fruit pure es, fruit preparations and jams.

Multivariate compositional analysis

Chemical parameters

Most attempts to determine the amount of fruit in processed fruit products have been based on the investigation of one or more fruit-specific constituents. The index compounds considered should show constant contents in the respective fruit species and should not be subject to alterations during processing. Variations in their contents are caused by a multitude of factors such as horticultural practices, variety, origin, and ripening stage of the fruits. As a consequence, a considerable amount of data needs to be compiled for statistical treatment, which is a prerequisite for the assignment of the probable limits of the values of the relevant constituents.

Goodall and Scholey (1975) employed multivariate statistical analysis including 23 parameters and a total of 54 samples of strawberries for the prediction of the fruit content and for authenticity control of fruit products. Compared to the use of only few compounds, an improvement in the estimates was achieved, and the highly significant correlations between pairs of parameters indicated that their ratios might be useful for the determination of fruit authenticity. Comprehensive investigations of fruits were performed including dry matter, ash, insoluble solids, weight of cores, malic acid, phosphorus, potassium, calcium and magnesium as index compounds (Prehn, Bosch, & Nehring, 1977a,b; Prehn & Nehring, 1977a,b; Prehn, Thaler, & Nehring, 1977). Despite the enormous data pool comprising 270 strawberry samples, 135 cherry samples, and 117 apricot samples, the 'ideal' marker compound could not be found. High variation coefficients as a consequence of biological heterogeneities necessitated the establishment of a statistical model. However, owing to the tedious statistical operations and unsatisfactory results, this method has not found acceptance.

Apart from jams, the determination of the fruit content of fruit preparations has always been a matter of intense research. Wallrauch (1995) considered the parameters citric, isocitric, and malic acids, as well as potassium, magnesium, phosphate, and the formol index, which were found to be subject to only minor variations. Data were collected from the most important strawberry cultivars and proveniences to deduce an equation for the calculation of the fruit content. Acceptable estimates were obtained for the fruit content of authentic strawberry pure es, provided that the parameters originate from the same fruits and interfering ingredients were not used. However, application of this formula to industrially produced fruit preparations led to overestimation of the fruit contents, due to the presence of indispensable ingredients such as colouring foodstuffs, sweeteners, thickeners, and consumable acids. Since corrections in the calculation of the fruit content are required, the applicability of the formula is restricted to fruit preparations of known composition, which is usually not the case.

Rheological parameters

In consideration to the limitations of multicomponent analysis based exclusively on chemical index parameters, further attributes were studied with respect to quality control of fruit derived products, such as the characterisation of their rheological behaviour. Costell, Carbonell, and Duran (1987) pointed out that the relationship between fruit content of jams and both specific fruit components and particular Rheological parameters could be a suitable approach to the estimation of the fruit weight. Fifteen strawberry jams with fruit contents ranging from 28 to 61% were examined including two chemical (Mg and N) and three rheological indices (yield stress and relation between two apparent viscosity parameters). The correlation coefficients between fruit content and these five parameters obtained by stepwise linear regression were higher (r2=0.897) than those obtained when chemical and rheological parameters were considered separately (r2=0.799 and 0.707, respectively). Significant differences of rheological parameters (Weltmann A and B constants, yield stress, flow behaviour) were found dependent on fruit content of jams from strawberry, peach, plum, and apricot (Carbonell, Costell, & Duran, 1991a). Beside components originating from the fruit, other ingredients such as sugar and pectin greatly affect the rheological behaviour of jams. Therefore, the influence of the main composition factors (fruit content, soluble solids and pectin) on the
rheological parameters of sheared jams was studied in order to determine their suitability for the estimation of the fruit content (Carbonell, Costell, & Duran, 1991b; Costell, Carbonell, & Duran, 1993). Strawberry and peach jams were selected representing different structures and textures of the respective fruit pulps. Time-dependent flow behaviour of sheared jams (Weltmann A and B) and yield stress calculated from measurements at low and medium shear rates, respectively, were considered in combination with the chemical parameters galacturonic acid content and soluble solids. The regression equations obtained allowed a prediction accuracy of 79.5 and 91.1% for the fruit content of strawberry and peach jams, respectively.

Index compounds

Organic acids and sugars

Organic acids in fruits exhibit a low susceptibility to changes during processing and storage, combined with an adequate stability compared to pigments and flavour compounds. Accordingly, their quantification and characterization appears to be suitable for the estimation of the amount of fruit as well as for the control of fruit authenticity. However, since organic acids are indispensable technological ingredients of most recipes, it becomes evident that this analytical tool is not applicable to jams and fruit preparations. Furthermore, depending on cultivar and degree of ripeness, organic acid contents are subject to considerable variations, thus limiting their applicability as a quantitative marker also in fruit juices and purees. Levels and ratios of certain organic acids such as quinic acid in cranberries and tartaric acid in grapes were found to be suitable markers for the detection of adulterations (Coppola & Starr, 1988). The organic acid profile also provides valuable information on the authenticity of apple juice (Wucherpfennig, 1976). Since only L-malic acid occurs naturally, the presence of D-malic acid indicates admixture of a synthetic malic acid racemate. Camara, Díez, Torija, and Cano (1994) concluded that the ratio citric/L-malic acid could serve as a reference index of authenticity for pineapple juices and nectars. Quinic acid, ascorbic acid, potassium and arginine were identified as specific marker compounds to prove the origin of kiwi puree (Castaldo, Lo Voi, Trifiro, & Gherardi, 1992). However, the estimation of the fruit amount in the kiwi products could not be accomplished. Citric acid was found to be a suitable marker to distinguish homemade from industrially produced quince jams (Silva, Andrade, Mendes, Seabra, & Ferreira, 2002).

Apart from organic acids, the sugar profiles were also used for the differentiation of fruit species, whereas their use as quantifiers of fruit contents is very limited. Identical sugar patterns were observed for fruits from various countries as well as for different varieties (Fitelson, 1970), which could be used for the detection of an illegal admixture of sugar solutions or fruit juices. Pilando and Wrolstad (1992) characterised non-volatile acids and sugars in combination with minerals and UV spectral profiles of commercial fruit juice concentrates to evaluate their quality and authenticity. Differences were monitored in the content of malic, fumaric and quinic acids between hard and soft pears, while sorbitol levels and glucose:fructose ratios allowed the discrimination of prune and pear.

Polyphenolics

Former studies focussed on the characterisation of phenolic compounds mainly for chemotaxonomic purposes. In recent years, improvements in instrumental analysis, in particular advances in liquid chromatography, provided detailed information on the profile of phenolic compounds and opened up new perspectives in the characterisation of fruits and derived products. Since the polyphenolic composition of fruits shows qualitative and quantitative differences depending, among others, on species, cultivar, and ripening stage, the determination of phenolic compounds is a useful tool for authenticity control of fruit based products and for the detection of fraudulent admixtures. Toma’s-Lorente, García-Viguera, Ferreres, and Tomàs-Barberán (1992) investigated the flavonoid profiles of commercial jams from apricot, peach, plum, strawberry, sour orange, apple, and pear. Since each jam showed a distinctive flavonoid pattern characterised by the presence of one or more markers, these compounds could be used for the detection of admixture of apple to apricot, peach, or pear jams by determination of the dihydrochalcone glycosides phloridzin and phloretin xyl glucoside. On the other hand, rutin proved to be characteristic of apricot and could therefore be used to prove the addition of apricot to peach jams. The flavonoid profile was also demonstrated to be suitable for authenticity control of citrus jams (García-Viguera et al., 1993), especially since the flavonoids were not affected by the manufacturing process. 5-O-caffeoylquinic acid and quercetin galactoside were the predominant phenolic compounds of quince jellies and jams (Silva et al., 2000). The influence of variety, maturity and processing on phenolic compounds of apricot jams and juices was studied by García-Viguera, Bridle, Ferreres, and Tomàs-Barberán (1994). While identical phenolic profiles were observed for all 11 apricot cultivars investigated, differences in the phenolic contents were found to depend on cultivar and maturity stage. Chlorogenic acid was the major phenolic compound, followed by the flavonoid quercetin.
rutinoside, smaller amounts of kaempferol rutinoside, and traces of other quercetin and kaempferol glycosides. Processing of apricots during jam and juice production did not change the qualitative phenolic composition.

It should be taken into consideration that improved analytical methods have extended our knowledge of the distribution of phenolic compounds in fruits and vegetables. Phloridzin and isorhamnetin 3-glucoside have long been considered typical of apple and pear, respectively, and have therefore been used as markers for the detection of fraudulent admixtures (Wald & Galensa, 1989; Versari, Biesenbruch, Barbanti, & Farnell, 1997). However, a number of very recent studies by LC–MS have revealed that phloridzin may also be found in minor amounts in strawberries (Hilt et al., 2003), rose hip (Hvattum, 2002), and artichoke (Sanchez-Rabaneda et al., 2003). Analogously, isorhamnetin glycosides have also been detected in several apple cultivars (Alonso-Salces et al., 2004; Schieber, Keller, Stricker, Klaiber, & Carle, 2002; Schieber et al., 2003). These results reveal a more widespread occurrence of phloridzin and isorhamnetin glycosides than previously assumed, and demonstrate the need of establishing more reliable markers for the control of the authenticity of fruits and derived products. Furthermore, it becomes evident that the determination of fruit contents based on polyphenolics is out of the question.

Anthocyanins

In addition to the phenolic compounds described above, anthocyanins have frequently been considered for authenticity purposes, since their specific patterns may allow the classification of fruit species and the detection of fraudulent admixtures of cheaper fruits or of fruits with a more stable colour. Especially in the case of strawberries, addition of coloring agents has often been reported, owing to the pronounced susceptibility of the pigments to degradation. The main anthocyanins of strawberries have been identified as pelargonidin 3-glucoside and cyanidin 3-glucoside (Lukton, Chichester, & Mackinney, 1955; Robinson & Robinson, 1932). Furthermore, the presence of pelargonidin 3-arabinoside (Fiorini, 1995), pelargonidin 3-O-(600-malonylglucoside) (Tamura, Takada, & Yoshida, 1995) and 3-(600-rhamnosylglucoside) of pelargonidin and cyaniding (Lopes da Silva, De Pascual-Teresa, Rivas-Gonzalo, & Santos-Buelga, 2002) has been demonstrated. Garcı’a-Viguera, Zafrilla, and Toma’s-Barbera’n (1997) examined anthocyanins as markers for the authenticity of processed products including fruit jams made from strawberry, blackberry, raspberry, blueberry, blackcurrant, and cherry. Despite losses of individual compounds amounting up to 40%, characteristic fingerprints for all jams could be obtained. Apart from pelargonidin 3-glucoside in strawberries, cyanidin 3-rutinoside and cyanidin 3-sophoroside were shown to be the main compounds of cherries and raspberries, respectively. The addition of blackberry containing cyanidin 3-glucoside as the main anthocyanin to the latter fruits could for instance be detected by shifts in the ratios of the marker substances. However, similar to the situation with the polyphenolics mentioned previously, more recent investigations have shown that strawberries also contain another anthocyanin with the novel aglycone which has been identified as 5-carboxypyrano-pelargonidin (Andersen, Fossen, Torskangerpoll, Fossen, & Hauge, 2004).

Furthermore, so far only cyanidin glycosides have been detected in black carrots (Gla’gen & Seitz, 1992; Gla’gen, Wray, Strack, Metzger, & Seitz, 1992), the concentrate of which is increasingly used as a coloring agent because of its pronounced stability. Using liquid chromatography–electrospray ionization multistage mass spectrometry, Kammerer, Carle, and Schieber (2003) recently demonstrated the presence of six acylated and non-acylated glycosides of peonidin and pelargonidin. As a consequence, the detection of small amounts of anthocyanins based on aglycones other than cyanidin in products made from black carrots cannot necessarily be attributed to a fraudulent admixture of other fruit or vegetable products. Apart from these new findings on the pigment profile, anthocyanins may also be subject to alterations during processing and storage. For example, marked changes and degradation of anthocyanins were observed during processing of blueberries and strawberries into juice and concentrate (Garzo’n & Wrolstad, 2002; Skrede, Wrolstad, & Durst, 2000), the extent of degradation being larger in concentrates than in juices. In particular, enzymation during processing may result in degrading anthocyanins patterns (Kammerer, Claus, Schieber, & Carle, 2005). During storage of black carrot juice, novel pyranoanthocyanins may also be formed through direct reaction of anthocyanins with hydroxycinnamates, i.e. caffeic, ferulic, and coumaric acids, as has only recently been shown by Schwarz, Wray, and Winterhalter (2004). Therefore, similar to other polyphenols, anthocyanins may only be used as quantitative markers in the quality control of fruit based products.

Infrared spectroscopy

The development of Fourier Transform Infrared (FTIR) spectroscopy operating in the mid-infrared region has opened up new perspectives in quality control for the food industry, because it allows a rapid screening and quantification of components
and therefore a high throughput of samples. The suitability of FTIR spectroscopy for the determination of the fruit content of jams produced from raspberry, apricot, and bramble was investigated by Wilson, Slack, Appleton, Sun, and Belton (1993). The dried jams were subjected to attenuated total reflectance (ATR) analysis using the potassium bromide pellet technique. In combination with partial least squares (PLS) regression a correlation of 0.94 was obtained between the weight of fruit and the area of a specific band at 1729 cm⁻¹, allowing the quantification of the fruit content of the jams. Furthermore, the tested fruits raspberry, apricot, and bramble gave rise to characteristic and reproducible diffuse reflectance spectra which could serve as fingerprints and thus provide perspectives for authentication. FTIR spectroscopy in combination with principal component analysis (PCA) and discriminant analysis (DA) was applied to the differentiation of purees from strawberry, raspberry, and apple using spectra recorded at 800–2000 cm⁻¹ for data analysis (Defernez, Kemsley, & Wilson, 1995). The purees could successfully be differentiated for both a calibration procedure and an independent data set validation. The method was also suitable for a more detailed discrimination of the fruits according to ripeness and state of freshness as examples. Defernez and Wilson (1995) analysed the FTIR spectra of jams to differentiate strawberry containing jams from those made without strawberry fruits. Using diffuse reflectance infrared spectroscopy (DRIFT) combined with DA, a classification of the jams into the two groups was accomplished with a success rate of almost 100%. However, the method required tedious sample preparation and still needed some improvement. FTIR spectroscopy and chemometrics as a means to detect the adulteration of strawberry and raspberry purees was extensively studied (Holland, Kemsley, & Wilson, 1998; Kemsley, Holland, Defernez, & Wilson, 1996). A database of a multitude of spectra of pure and adulterated purees was collected and subjected to PLS regression. Confidence intervals of 94.3 and 95%, respectively, were found for the prediction values of pure strawberry and raspberry purees. Adulterated strawberry purees were prepared by the admixture of apple and plum, and glucose and sucrose solutions, grape juice and rhubarb compote, while adulteration of raspberry purees included sucrose as well as apple and plum puree. These adulterants could clearly be detected down to levels to be expected for adulterated purees on the market, with estimated detection limits of 20% (w/w) for apple and plum and 4% (w/w) for sucrose. Contai, Leo’n, and Downey (2002) developed a model to confirm the authenticity of purees of raspberry and strawberry and to quantify the apple content in adulterated samples based on near infrared (NIR) and visible spectroscopy. Best models allowed rapid detection of apple adulteration at levels greater than 20% (w/w, strawberry) and between 10 and 20% (w/w, raspberry). PLS regression was used for the quantification of the extrinsic fruit content, resulting in prediction errors of 3.4 and 5.5% for apple in raspberry and strawberry purees, respectively. Downey and Kelly (2004) recently conducted studies on sulfited strawberry and raspberry purees adulterated with cooking apple using visible and NIR spectroscopy. Classification and quantification models were developed revealing that the soft independent modelling of class analogy was sufficiently accurate to indicate pure strawberry purees (classification rate of 95.1%). Apple content was determined using PLS regression with minimal detection levels of approximately 25 and 20% (w/w) obtained for raspberry and strawberry purees, respectively.

**PCR methods**

Species determination using PCR methods is well established for foods containing DNA in detectable amounts, particularly meat and fish. In contrast, comparatively few studies have so far been conducted on the application of DNA and proteins to authenticity and quality control of fruits and derived products. Distinctive genomic fingerprints of apples were analysed by Morton, Adams, and Barbara (1993) using PCR and agarose gel electrophoresis. This rapid method required only little DNA and allowed the differentiation and identification of apple cultivars independent of morphological characteristics of the fruits. An analytical approach for the detection of the adulteration of orange juice by PCR technique was developed by Knight (2000), providing a quantification of 2.5% mandarin juice in orange juice. Although the applicability of DNA analysis to the authentication of processed fruit products, in particular after intensive heat treatment, was shown to be limited because of the DNA degradation, particularly in acidic media (Bauer, Weller, Hammes, & Hertel, 2003; Hufner, Hotzel, Sachse, & Engel, 1998), recent studies revealed that qualitative PCR may also be feasible for authenticity control even in jams, fruit preparations and fruit yogurts (Mulleder, 2003; Popping, 2002).

**Mass spectrometry and NMR spectroscopy**

Although instrumental authentication techniques including MS and NMR methods are primarily utilised for the detection of adulterations of fruit juices, a brief survey is given in this section since an application to purees is at least conceivable. The relevance of MS and NMR methods to food authenticity is reflected by a number of recently published reviews (Alberti, Belton, & Gil, 2002;
Isotope ratio mass spectrometry (IRMS) was used to characterise the specific natural isotope profile (SNIP) of C4 derived sugars as well as organic acids in order to detect a fraudulent addition to authentic fruit juices and concentrates (González, Remaud, Jamin, Naulet, & Martin, 1999; Jamin et al., 1997). The potential of pyrolysis mass spectroscopy coupled with multivariate analysis for the determination of origin and for the indication of adulterations of juices on the basis of sucrose was reported by Garcia-Wass, Hammond, Mottram, and Gutteridge (2000). Applications of NMR spectroscopy to authenticity control of fruits and fruit containing products is limited to liquid samples such as juices and purees. Characterisation and differentiation of raspberry, strawberry, and plum purees by means of spectra obtained from HNMR was found to be a promising approach (Colquhoun, 1998). Moreover, multivariate analysis allowed the discrimination of adulterated and pure purees. An important contribution to the analytical tools for food authentication is made by the selective natural isotope fractionation (SNIF)-NMR method. Complementing SNIF-IRMS, this technique permitted the detection of added C3 derived sugars and acids in fruit juices (Martin, 1998).

Vanilla extract is an extremely costly constituent of fruit preparations which is often replaced by natural or synthetic vanillin. Since the genus Vanilla follows the CAM photosynthetic pathway, its typical 13C/12C isotope ratio allows the detection of admixtures derived from petrochemical or different natural precursors like eugenol, guajacol, and lignin from C3 plant sources (Bricout, Fontes, & Merlivat, 1974; Hoffmann & Salb, 1979). As demonstrated for volatile oils, isotope ratio mass spectrometry and 2H NMR determination of site specific natural isotope fractionation provide powerful tools for the detection and even a quantitative determination of adulterants (Carle, Beyer, Cheminat, & Krempp, 1992; Carle, Fleischhauer, Beyer, & Reinhard, 1990).

Miscellaneous methods

While most studies on quality and authenticity control of fruit purees, jams and related products have so far utilized low-molecular compounds and spectrometric data, only little attention has been paid to polymeric constituents of the fruits. The polysaccharide composition of fruit juices was previously studied with respect to the detection of adulterations and to an estimation of product quality. Soluble polysaccharides of orange juices were isolated by precipitation using ethanol (Kauschus & Thier, 1985). Subsequent hydrolysis and determination of the monosaccharides provided characteristic patterns which were independent of different proveniences and could therefore serve as fingerprints. In contrast, inconsistent sugar profiles obtained from hydrolysed colloids of pineapple juices were found, originating from different proveniences and ripening stages of the fruits (Will, Herberth, & Dietrich, 1994). Cell wall polysaccharides were recently proved to be suitable as quality and authentication markers of fruit purees and fruit preparations (Fügel, Carle, & Schieber, 2004). They were extracted by precipitation with ethanol and separated into different pectin fractions, hemicellulose and cellulose. Within the respective fruit species characteristic neutral sugar profiles of the fractions were determined, revealing that the method may be helpful for the differentiation of fruit species as well as for the detection of a fraudulent admixture of non-declared fruits. Moreover, hemicellulose contents in the fruits proved to be constant, offering perspectives for the determination of the fruit content of complex fruit products such as fruit preparations, jams, and spreads. For strawberry and cherry fruit preparations of various compositions, an excellent agreement between specified and determined fruit contents could be obtained in most cases (Fügel, Schieber, & Carle, in press; Schieber, Fügel, Henke, & Carle, 2005).

Recent findings demonstrated that aroma volatiles of fruits may also allow the detection of admixtures of apple to soft fruit purees. The compounds were extracted from pure and adulterated strawberry purees using solid-phase microextraction followed by gas chromatographic analysis (Reid, O’Donnell, & Downey, 2004). Principal component analysis was conducted on 37 aroma volatiles which were supposed to be relevant for differentiation of adulterated and pure samples. Compounds showing the greatest influence on the results were identified as the key aroma components of apples (hexanoic acid, 2-hexenal, and a-farnesene). Quantification of apple puree was achieved with a standard error of 11.6%, implying a minimum detectable level of 25% (v/v). The extension of this technique to industrial settings is aspired in future studies.

Conclusions

Considering the recently established regulatory guideline improving consumer protection, the urgency for the development of justiciable methods to evaluate quality and authenticity of foods becomes apparent. Article 7 (EU directive 79/112/EEC) as amended in the EU directive 97/4/EC prescribes the labelling of foods and beverages according to the ‘quantitative ingredient declaration’ (QUID). For compositional foodstuff (e.g. jams, spreads, fruit containing dairy products), ingredients are to be listed on a quantity base,
particularly when emphasised in words, pictures or graphics and when they forming part of the name under which the product is sold. From the numerous investigations described previously, it becomes evident that tremendous efforts have been made in quality and authenticity control including the evaluation of the fruit content of pure’és, jams, and fruit preparations. On the other hand, each analytical approach has its limitations which restrict its applicability. It would be highly desirable to have a simple, rapid, and generally available tool for the detection and quantification of fraudulent manipulations of food. New methods for the detection of adulterations will almost inevitably bring up new, more sophisticated ways of adulterations, and it would be na’’ve to believe that the fantasy of fraudulent persons has come to an end. Therefore, it is hoped that through the availability of novel analytical approaches the expense necessary for adulterating food will be increased at a level which makes fraud extremely risky and increasingly uneconomical.

References


cultivars and species. BCPC Monograph, 54, 289–294.


2. Experimental section

2.1 HPLC analysis and determination of saccharides

The following carbohydrates have been analyzed: glucose, galactose, raffinose, fructose, mannitol, sorbitol, lactose, maltose, cellobiose, and sucrose. Food carbohydrates are characterized by a wide range of chemical reactivity and molecular size. Because carbohydrates do not possess chromophores or fluorophores, they cannot be detected with UV-visible or fluorescence techniques. Nowadays, however, refractive index detection can be used to detect concentrations in the low parts per million (ppm) range and above, whereas electrochemical detection is used in the analysis of sugars in the low parts per billion (ppb) range.

Sample preparation

Degassed drinks can be injected directly after filtration. More complex samples require more extensive treatment, such as fat extraction and deproteination. Sample cleanup to remove less polar impurities can be done through solid-phase extraction on C18 columns.

Figure 1 Scheme of HPLC apparatus (Gratzfeld, 2001).

Figure 2 HPLC analysis of carbohydrates in lemonade and corn extract (Gratzfeld, 2001).
CALIBRATING CURVES

FRUCTOSE

Table 1 Concentration values and peak area for fructose

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<td>3.044</td>
<td>584.482</td>
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Figure 3 Fructose calibration curve

GLUCOSE

Table 2 Concentration values and peak area for glucose

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SUCROSE

Table 3 Concentration values and peak area for sucrose

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<td>398.254</td>
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NOTES: Formula of straight line is given by followed formula: \( y = ax + b \), \( R^2 \)

SAMPLE PREPARATION:

Samples: carrot juice, cabbage juice, apple juice and stewed fruit (preserved fruit) syrup from apples were prepared from commercially buy samples. After the preparation of juices in Moulinex juicer apparatus we isolate the juice and the samples were further analysed.
10 ml of sample was measured and inject to 100 ml bank. We added approximate 60 ml deionized water, mixed it and step by step was added 5 ml Carrez reagent I again mixed and 5 ml Carrez reagent II and also mixed (Príbela, 1991). Samples were coagulated, volume was added to 100 ml with deionized water, mixed and finally we filtrated it over folded paper. Filtrate was analyzed on HPLC. Before analyze we filtrated samples again through microfilter (Lefebrvre et al., 2002).

Sample preparation for pulping apples:

Apples were purchased from local market. 10 g mixed pulping apples (sample) was measured and inject to 100 ml bank. We added approximate 60 ml deionized water mixed it and bring to sonic bath for 30 minutes. After that step by step was added 5 ml Carrez reagent I again mixed and 5 ml Carrez reagent II a also mixed. Samples were coagulated, volume was added to 100 ml with deionized water, mixed and finally we filtrated it over folded paper. Filtrate was analyzed on HPLC. Before analyze we filtrated samples again through microfilter (Lefebrvre et al., 2002).

LIST OF USED INSRUMENTS:

HPLC – high-pressure liquid chromatograph apparatus
pump Delta Chrom™ SDS 030
RI detector K/2301 (KNAUER, Germany)
microfilters ProFill, 25mm HPLC Syringe Filter, Nylon (PA)
ultrasonic bath, type UC 002 BM1, (Tesla Stropkov, Slovak republic)
column Nucleodur 100-5 NH₂ – RP (250 x 4 mm) (Düren, Germany)
Controller data evaluation with program Clarity version 2.4.1.56

CONDITIONS BY MEASUREMENT:
Temperature: laboratory
Detection: RI detector

![CHROMATOGRAMS](image)

Figure 6 Chromatogram of apple juice (retentive times for Fructose = 6.82 min, Glucose = 7.69 min, Sucrose = 10.74 min).
Figure 7 Chromatogram of cabbage juice (retentive times for Fructose = 6.77 min, Glucose = 7.61 min, Sucrose = 10.64 min).

Figure 8 Chromatogram of carrot juice (retentive times for Fructose = 6.81 min, Glucose = 7.64 min, Sucrose = 10.69 min)
Figure 9 Chromatogram of stewed fruit syrup from apples (retentive times for Fructose = 6.71 min, Glucose = 7.58 min, Sucrose = 10.68 min)

Figure 10 Chromatogram of pulping apples (retentive times for Fructose = 6.70 min, Glucose = 7.57 min, Sucrose = 10.64 min)

RESULTS AND DISCUSSION:

Table 4 Peak area and saccharides concentration in the samples

<table>
<thead>
<tr>
<th>Sample/Peack Area</th>
<th>Fructose – Peak Area (mV.s)</th>
<th>Glucose – Peak Area (mV.s)</th>
<th>Sucrose – Peak Area (mV.s)</th>
<th>c Fructose (g / 100 cm(^3))</th>
<th>c Glucose (g / 100 cm(^3))</th>
<th>c Sucrose (g / 100 cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cabbage juice</td>
<td>507.1</td>
<td>662.12</td>
<td>156.26</td>
<td>2.74</td>
<td>3.69</td>
<td>0.90</td>
</tr>
<tr>
<td>Apple juice</td>
<td>1423.65</td>
<td>486.5065</td>
<td>336.39</td>
<td>7.60</td>
<td>2.73</td>
<td>1.82</td>
</tr>
<tr>
<td>Carrot juice</td>
<td>159.77</td>
<td>228.58</td>
<td>817.75</td>
<td>0.90</td>
<td>1.32</td>
<td>4.29</td>
</tr>
<tr>
<td>Stewed fruit syrup from apples</td>
<td>1449.13</td>
<td>1225.04</td>
<td>3824.17</td>
<td>7.73</td>
<td>6.77</td>
<td>19.71</td>
</tr>
</tbody>
</table>

Table 5 Peak area and saccharides concentration in the sample of pulping apples

<table>
<thead>
<tr>
<th>Sample/Peack Area</th>
<th>Fructose – Peak Area (mV.s)</th>
<th>Glucose – Peak Area (mV.s)</th>
<th>Sucrose – Peak Area (mV.s)</th>
<th>c Fructose (g / 100 g)</th>
<th>c Glucose (g / 100 g)</th>
<th>c Sucrose (g / 100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulping apples</td>
<td>1380.85</td>
<td>994.75</td>
<td>4227.51</td>
<td>7.37</td>
<td>5.51</td>
<td>21.77</td>
</tr>
</tbody>
</table>
Example of calculation:
- for glucose in the cabbage juice

Formula from the calibrating curve of glucose:

\[ y = 188.59x + 9.5328 \]

Peak Area for Fructose = 507.1 mV.s…………… (=y)

Than from formula \( x = 2.74 \text{ mg cm}^{-3} \)

In 100 ml it is \( x \times 100 = 274 \text{ mg} / 100 \text{ cm}^3 \)

Because in our storage solution was 10 ml juice in 100 ml flask, therefore 274 mg glucose is in 10 ml juice. It is mean, that in the 100 ml of juice will be 2740 mg glucose (= 2.74 g).
2. 2 ITP analysis and determination of mineral elements

Isotachophoresis (figure 12) has been performed in capillaries for decades and instruments for cITP (figure 13) have been commercially available since 1974. In isotachophoresis, the sample zone is sandwiched between a leading and a terminating electrolyte in the capillary. The leading electrolyte is chosen so that it has a higher mobility than any other compound in the capillary, and in the same manner the terminating electrolyte is selected to have the lowest mobility. Solutes in the sample zone will migrate according to their intrinsic mobilities, and as individual solute zones are formed discontinuities in electric field strength will appear in the zone between the electrolytes. Cationic and anionic analytes have to be determined in different runs, because the electrolyte compositions will have to be different, and neutral compounds cannot be separated (Lindenberg, 1996).

Figure 12 Capillary isotachophoresis instrument

An isotachophoretic method was developed for the determination of organic and inorganic acids (benzoic, citric, formic, fumaric, lactic, malic, phosphoric and tartaric acid) in feed additive preparations (Blatný at al., 1996). cITP was used for determination of the anionic profile of orange juice, sulphite in mustard, fumaric acid in apple juice and fluoride in feed mixtures (Szlik et al., 2005).
Qualitative and Quantitative analysis

Quantitative analysis
For the quantitative determination of ionic species by isotachophoresis, calibration graphs can be obtained experimentally. Theoretically, there should be a linear relationship between the length of the zone (l_x, l_{sx}) of a specific ionic species and the amount of the ionic species introduced. Calibration graphs for all ionic species present in a sample that are required to be separated must be measured, however (Everaerts et al., 1974).

Qualitative analysis
Into the figure 14 we can see isotachoforegram, when:
At qualitative analysis we use conception RSH value (Relative Step Height). It is a quantity of dimension one. This value is constant for substance. Calculated it follow:

$$RSH_X = \frac{(h_X-h_L)}{(h_T-h_L)}$$

**Determination of cations in fruit and vegetable juices using ITP**

**Conditions:**

**Leading electrolyte:**
- H2SO4 7,5.10⁻³ mol.dm⁻³
- 18-Crown-6 7.10⁻³ mol.dm⁻³
- Additive 0,1 % MHEC (methyl 2-hydroxyethyl cellulose)

**Terminating electrolyte:**
- BTP (bis tris propane) 10.10⁻³ mol.dm⁻³
- Acetic acid 20.10⁻³ mol.dm⁻³

**Current in pre-separation part:** 200 µA

**Current in separation part:** 30 µA

**Detection:** conductometry

**Time analysis:** 45 min

**Instrument:**
- Electrophoretic analyzer EA 102 (Villa Labeco, Špiská Nová Ves), software ITP Pro 32 Version 1.0.4.26

**Sample preparation:**
- 10 ml juice (carrot, apple, cabbage) was diluted in redestilation water in to the 100 ml flask. This solution was filtered and injected into the ITP.
Calculations:
From linear equation \((y=ax+b)\) deliverance \(x\) volume \((x=(y-b)/a)\) and substitute into the equation:
\[ c = x\cdot M\cdot f\cdot z \]
where:
c – concentration substance in to the sample
M – molecular weight of pure substance
f – conversion factor: \(f = M/M_{salt}\)
z - dilution

Results and discussion:

Table 6 Content of Ca in juice

<table>
<thead>
<tr>
<th></th>
<th>(y_1) (mm)</th>
<th>(y_2) (mm)</th>
<th>(y) (mm)</th>
<th>(c_1) (g.dm(^{-3}))</th>
<th>(c_2) (g.dm(^{-3}))</th>
<th>(c) (g.dm(^{-3}))</th>
<th>RSH(_1)</th>
<th>RSH(_2)</th>
<th>RSH</th>
</tr>
</thead>
<tbody>
<tr>
<td>carrot</td>
<td>10,25</td>
<td>10,45</td>
<td>10,35</td>
<td>8,2673.10(^{-3})</td>
<td>0,000147</td>
<td>0,000115</td>
<td>0,623</td>
<td>0,624</td>
<td>0,623</td>
</tr>
<tr>
<td>apple</td>
<td>20,5</td>
<td>5,1</td>
<td>12,8</td>
<td>0,003396686</td>
<td>-0,00158</td>
<td>0,000907</td>
<td>0,663</td>
<td>0,664</td>
<td>0,663</td>
</tr>
<tr>
<td>cabbage</td>
<td>11</td>
<td>26,65</td>
<td>18,825</td>
<td>0,000325161</td>
<td>0,005385</td>
<td>0,002855</td>
<td>0,658</td>
<td>0,658</td>
<td>0,658</td>
</tr>
</tbody>
</table>

Figure 15 Calibration curve for Ca

Content of Na and K in juice

Table 7 Content of Na in juice

<table>
<thead>
<tr>
<th>Na</th>
<th>(y_1) (mm)</th>
<th>(y_2) (mm)</th>
<th>(y) (mm)</th>
<th>(c_1) (g.dm(^{-3}))</th>
<th>(c_2) (g.dm(^{-3}))</th>
<th>(c) (g.dm(^{-3}))</th>
<th>RSH(_1)</th>
<th>RSH(_2)</th>
<th>RSH</th>
</tr>
</thead>
<tbody>
<tr>
<td>apple</td>
<td>183,35</td>
<td>23,75</td>
<td>103,55</td>
<td>0,053322083</td>
<td>0,023036</td>
<td>0,038179</td>
<td>0,529</td>
<td>0,561</td>
<td>0,54</td>
</tr>
<tr>
<td>cabbage</td>
<td>25,6</td>
<td>25,45</td>
<td>25,525</td>
<td>0,023386965</td>
<td>0,023359</td>
<td>0,023373</td>
<td>0,558</td>
<td>0,554</td>
<td>0,55</td>
</tr>
</tbody>
</table>

Na and K go like mixture peak, because they have very near mobilities.
Figure 16 Calibration curve for Na

Figure 17 Ca content in the samples of juices

Figure 18 Na and K content in the samples of juices
Appendices:

Carrot juice

LE - leading electrolyte
I - Ca
TE - terminating electrolyte

Apple juice
LE – leading electrolyte
2 – Na+K
3 – Ca
TE – terminating electrolyte

Cabbage juice

LE – leading electrolyte
2 – Na
3 – Ca
TE – terminating electrolyte
2. 3 Thermosterilization process of apple sauce

Material and methods:
Apples were obtained from local market. After washing, apples were dehulled and sliced on equivalent pieces. Then we put 300 g of apples in glass and water (400 ml), sugar (40 g) and lemon acid (one third of coffee spoon) were added. The glass was closed and put in the boiling water bath and the sterilization process began. We noticed every minute the temperature inside the glass and in the water bath. Obtained data are shown in Table 8.

Table 8 Measured and computed data from the sterilization process

<table>
<thead>
<tr>
<th>Time [min]</th>
<th>Temp. [°C]</th>
<th>log(U)</th>
<th>U</th>
<th>I/U</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>57.2</td>
<td>1.97726</td>
<td>94,89866</td>
<td>0.010538</td>
</tr>
<tr>
<td>1</td>
<td>59.1</td>
<td>1.859853</td>
<td>72,41907</td>
<td>0.013809</td>
</tr>
<tr>
<td>2</td>
<td>61.9</td>
<td>1.686832</td>
<td>48,62189</td>
<td>0.020567</td>
</tr>
<tr>
<td>3</td>
<td>63.6</td>
<td>1.581783</td>
<td>38,17538</td>
<td>0.026195</td>
</tr>
<tr>
<td>4</td>
<td>65.2</td>
<td>1.482914</td>
<td>30,40284</td>
<td>0.032892</td>
</tr>
<tr>
<td>5</td>
<td>66.9</td>
<td>1.377866</td>
<td>23,87073</td>
<td>0.041892</td>
</tr>
<tr>
<td>6</td>
<td>68.5</td>
<td>1.278996</td>
<td>19,01063</td>
<td>0.052602</td>
</tr>
<tr>
<td>7</td>
<td>70</td>
<td>1.186307</td>
<td>15,35701</td>
<td>0.065117</td>
</tr>
<tr>
<td>8</td>
<td>71</td>
<td>1.124513</td>
<td>13,32028</td>
<td>0.075073</td>
</tr>
<tr>
<td>9</td>
<td>72</td>
<td>1.06272</td>
<td>11,55367</td>
<td>0.086553</td>
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<tr>
<td>10</td>
<td>72.9</td>
<td>1.007106</td>
<td>10,16497</td>
<td>0.098377</td>
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<tr>
<td>11</td>
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<td>0.110237</td>
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<tr>
<td>12</td>
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<td>7,981007</td>
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<tr>
<td>13</td>
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<td>7,122347</td>
<td>0.140403</td>
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<tr>
<td>14</td>
<td>76.2</td>
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<tr>
<td>15</td>
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</tr>
<tr>
<td>16</td>
<td>77.9</td>
<td>0.69814</td>
<td>4,990454</td>
<td>0.200383</td>
</tr>
<tr>
<td>17</td>
<td>78.4</td>
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<td>4,647757</td>
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</tr>
<tr>
<td>18</td>
<td>78.9</td>
<td>0.636347</td>
<td>4,328593</td>
<td>0.231022</td>
</tr>
<tr>
<td>19</td>
<td>79.4</td>
<td>0.60545</td>
<td>4,031347</td>
<td>0.248056</td>
</tr>
<tr>
<td>20</td>
<td>79.8</td>
<td>0.580733</td>
<td>3,808315</td>
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</tr>
<tr>
<td>21</td>
<td>80.2</td>
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<td>3,597622</td>
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<tr>
<td>22</td>
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<tr>
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<td>80.8</td>
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</tr>
<tr>
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<td>81.2</td>
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<td>3,120487</td>
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<tr>
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<tr>
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<td>0.469505</td>
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<tr>
<td>27</td>
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<td>0.450967</td>
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<tr>
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<td>82.2</td>
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<td>0.369463</td>
</tr>
<tr>
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<td>82.4</td>
<td>0.42007</td>
<td>2,630695</td>
<td>0.380128</td>
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<tr>
<td>30</td>
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<td>0.401532</td>
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<tr>
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<tr>
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</tr>
<tr>
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<tr>
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<tr>
<td>36</td>
<td>78.1</td>
<td>0.685781</td>
<td>4,850443</td>
<td>0.206167</td>
</tr>
</tbody>
</table>
Results and discussion:
From our measured data we achieved the graphical relationship between 1/U value and time, which is shown in Figure 1. After the integration of the area under curve we obtained value 7.70. Then we find unit area, which is displayed in the graph with red rectangle and its area reach 8.00. The value W involve the condition, if the sterilization process was sufficient or not. The W value was calculated by the ratio of obtained area under the curve and the area which occupy unit area. If the W is greater than 1, the sterilization process is sufficient. The value of W in our measurement was 0.9625 (7.7/8 = 0.9625), what means, that the sterilization process was insufficient.

Conclusion:
After the computing of W value we recognized, that our sterilization process was insufficient. The solution may be in the prolongation of the heating time in the maximum temperature rate (approximately about 2 or more minutes). Another possible solution may be in the application of higher temperature during the sterilization process.
REFERENCES:


