2012 International Conference on Environmental, Biomedical and Biotechnology
IPCBEE vol.41 (2012) © (2012) IACSIT Press, Singapore

The Problem of Falsification of Citrus Juices and Methods of Its Detection

Miranda Gorgiladze, Eter Nizharadze, Guram Papunidze, Tamaz Shavadze and Sopiko Tskvitinidze

Batumi Shota Rustaveli State University

Abstract. The identification of naturalness has a great significance in evaluating the quality of food products because the violation of naturalness is the same as falsification. There are various ways of falsifying food products: the alteration of expensive food products with cheaper ones, production of low food value products, changing recipe, misappropriation of trade names that misleads the consumer to estimate the food quality and variety.

Keywords: Naturalness, Falsification, Orange juice, Amine nitrogen, Number of Chloramines, Proline, Formolite number, Amino acid.

1. Introduction

On the one hand, the technology of producing citrus juices is violated during the falsification that causes the plunder of state property and is considered as a criminal offence.

On the other hand, the falsification of citrus juices may be related to inputting harmful substances for human organism into juices. For example, inputting tartaric acid or synthetic citric acid into citrus juices as well as various colouring agents, emulsifiers, synthetic amino acids and others, that causes the ecologically contaminated foodstuff production.

The falsification reaches the particular large scale in the production of juice concentrates when it is possible to change the entire fruit with the extraction.

2. Methods of Falsification

The problem of falsification of citrus juices was first discussed publicly on international congress held in Catania in 1959. Since about 1960, a lot of data on falsification of citrus juices have appeared in special foreign literature. It should be mentioned here the scientific works of Kalvarono and Di Jiakomo (Italy), Primo and Royo (Spain), Benk and Koch (Germany), Vanderkuk and Iakoiama (USA), Keford and Chandler (Austria) [1].

The most widespread ways of citrus juices falsification may be divided as follows:

- Adding substances of natural juices from outside (water, citric acid, ascorbic acid, etc);
- Adding the substances into juice that don't contain these substances (colouring agents, artificial emulsifiers, tartaric acid and so on);
- Adding other citrus juices (e.g., adding the extract of peel of lemon or grapefruit into tangerine juice).

The analytical methods of detection of the falsification may be divided into the 3 groups:

The first group includes the quantitative determination of components characterized for the given juices.

The second group includes the qualitative analysis methods those give opportunity to detect the foreign substances added in foodstuff;

The third group includes the methods which give opportunity to detect the extract of other juices or peel added in the given juice.

The initial form of citrus juices falsification was the dilution with sugar syrup and the addition of organic acids and colouring agents. Despite this, such kind of falsification is very primitive, it is impossible to discover it applying such modern methods as the gas-liquid chromatography. To be more precise, organic acid and sugar in juice can be available via gas-liquid chromatography, but it is impracticable to determine if they were artificially added into the juice or they were just natural components. Therefore, it was essential to establish such characteristics of naturalness that would be impossible to discover.

It should be noted that in many cases the falsifiers continually watch the scientific achievements in the field of falsification and look for the contradictory methods. For example, when scientists used the amino acids in order to discover falsification (it should be noted that citrus juices contain about 20 kinds of amino acids that are in juice in different ratios), the falsifiers produced tablets which contained amino acids with the same name and ratio as citrus juices. The juices were falsified by adding such tablets.

It is worth to denote that the laboratory of juice factories is often equipped with the modern equipment. 20 employees work for the laboratory, among them 2-3 are the representatives of arbitrary service. Laboratory staff has developed so-called "circulars" that contain the limited amount of characteristics that are the juice. In any case, during the juice production, they check the meanings of these characteristics in order to determine the falsification of juice and point on the labels. If even one meaning of characteristics is not suitable to mentioned meaning on the label during checking juice, then we have the fact of violating the naturalness or falsification.

3. Characteristics of Citrus Juice Naturalness

There are different characteristics of citrus juice naturalness. For example, some researchers suggest the ration of izocitric acid and citric acid to discover the falsification. It is estimated that composition of natural juices consists of izocitric acid and its existence in the juice points on the usage of synthetic citric acid. It is established that the ratio of citric acid and izocitric acid is invariable and equals to 200 [2-4].

The nitrogenous compounds are into the composition of citrus juices. Their content consists of 10 % of the soluble substances. It should be mentioned the amino acids, proteins, amines and amides among the nitrogenous substances. The soluble amino acids are very significant among the major nitrogenous substances. The determination of total nitrogen with the usage of Keldal method contains the abovementioned components and the quantitative index of juice is characterized with it. The study of amino acids has got a special meaning for controlling of the citrus juices. A number of works has been dedicated for studying this issue /5-7/.

Nowadays, the formolite number (amino nitrogen) is widely used. It is considered by the majority of authors that formal number is not sufficient to establish the falsification. Therefore they suggest conducting the typical chromatography of amino acids with the formal number [8-13].

3.1. Chemical Components

Proline is one of the significant amino acids. Some of the authors suggest the ratio of proline and formaline for the discovery of falsification during the process of quality assessment of citrus. Dilution of juices with water and citric acid reduces the content of proline and formaline, but it can’t change their ratio [14-17].

The ash content and sugarless extraction belong to a generally accepted indicator of the quality of juices [18].

The ratio of potassium and sodium is also used because of the content of natrium is 20-50 times higher in the artificially produced juices than in natural juices. Besides this, nonexistence of potassium is characterized with the synthetic juices.

As it is known, the cheapest and simplest method of citrus juice falsification is to add water into juice. Consequently, the content of organic part of juice is reduced and inorganic or mineral part is increased. Hereby, the addition of water is determined by using of its mineral components which are composed of large quantities of water content, but their content is minimal in citrus juices. Nitrates and phosphates belong to

such components. The high concentration of nitrates in orange juices indicates on the addition of the drinking water containing nitrates [9-12].

As mentioned above, one of the ways of falsification is to use the extraction of peel. The peel extraction contains the some amounts of soluble dry substances that are similar to the juice of dry substances with chemical composition and physical features. The peel extract supplementation is determined by specifying B_1 vitamin, hesperedine and pectin. The high contents of pulp and pectin in small quantity indicate the falsification. It was also established that it is not feasible to determine carotene during the control of juice quality [23].

Ultraviolet absorption of juices and usage of spectra of radiation are discussed for discovering peel extract in juice. It is established that peel extract shows a weak visible absorption (465, 443, 425 nm) and stronger ultraviolet absorption (325,280 and 245 nm) than natural juice does [24-28].

Number of chloramines belongs to one of the characteristics of the juice naturalness. It contains phenolic and other easily corrosive components. This does not include organic acids and sugars [29.30].

Some of the authors used microbiological methods for discovering falsification [31-32].

It is established that supplementation of seed plants juices or grapes juices into the citrus juices may be discovered according to the content of leikoantocyanes or tartaric acids. It is estimated that orange juices don't include leikoantocyanes, their content in apple juice ranges from 100-400mg/dm^3, in grape juice it ranges from 200 to 300 mg/dm^3 [33].

4. Statistic Methods of Determining the Citrus Juice Quality

The variation coefficients, standard deviation, limited meanings of components of juice are used to determine the citrus juice quality. Some authors don't agree the determination of only minimal or maximal meanings of juice components. They underline that these data are not only insufficient, but in most cases it is incorrect because if they are changed in large extent with dilution of juices 1:1, then their meanings, without inputting any synthetic additives from outside, will be inputted into the limited frontiers of meanings. In this case the falsified juice may be considered as natural. Hereby, the authors offer the determination of equality index of juice with limited meanings [34-37].

The difficulty of selecting ration of one component or two and three components has made it required to use the statistical methods based on quantitative relationship of fruit components.

Currently, the equations are being developed that are characterized for the composition of citrus juices. The main objective is to develop such equations which will be useful for identifying falsification [38-44].

5. New Methods of Determination of Tangerine Juice Naturalness

We have developed the methods of determination of tangerine juice naturalness [45]. Where the total and amino nitrogen and their ratio, ash content, its alkalinity, the number of chloramines, massive concentration of proline are used as characteristics of naturalness. These characteristics satisfy all requests towards the characteristics of naturalness. They have a low coefficient of variation: they are thermostable, are slightly changed during juice processing and storage, with dependence on the conditions of soil-climate. All parameters, besides proline, are changed during the process of maturing. The content of proline increases during the process of fruit maturing.

It is determined how the formal number is in tangerine juice changed with supplementation of amino acid [46].

The spectrophotometric method of analysis has been developed for discovering of additives in tangerine juice [47].

The linear regressive models of tangerine juice composition have been developed on the base of the multiple correlation analysis method and also statistic test of their usage has been developed. It is possible to determine the naturalness of fresh juice and falsified juice by using it if the meanings of control characteristics are within the limits of their natural fluctuation [48].

6. References

[1] Petrus D.R., Dougherty M.H. *Spectophotometric analyses of orange pulp washes* // J. Food Sci. -1973. – Vol. 38, №5. – p.913_914;

[2] 65. Rother H., Heidelberg K. *Die Iso- Zitronensaure in der Getrakeindustrie* // Flüss. Obst. – 1976.Bd. 43, №8. – s. 319- 32;

[3] Ara V., Török M. Statistische *verfahren als Entscheidungshilfe bei der Beurteilung der Reinheit von Orangensäften* // Ind. Obst. und Gemüseverwetung. – 1980. – Bd. 65, №12. – a. 297-300.

[4] Ara V., Török M. *Statistische verfahren als Entscheidungshilfe bei der Beurteilung der Reinheit von Orangensäften* // Ind. Obst. und Gemüseverwetung. – 1980. – Bd. 65, №12. – a. 297-300.

[5] Aurelio F. *Osservazioni sul numero di formolo quale metodo per dosare la quantita di succo presente nelle bibilte* // Essenze deriv. argum. – 1975. – Vol. 45, №3-4. – p. 308-314;

[6] Bellomo A., Licastro F., Kunkar A. *Numero di formolo azoto totale/azoto amminico: unnuovo indice azotato per il controllo di qualita dei succhi di agrumi* //Rassegna Chimica. – 1971. - №1. – P. 14-18;

[7] Benk E. *Der Chloraminwert als Kennazhl der Fruchtsaft- Untersuchung* // Flüss. Obst. – 1960. – Bd. 27, №3.- s.12-13;

[8] Benk E., Cutka J., Bergmann E. Der. *Nitratgehalt als analytische Kennzahl fur die Beurteilung von Orangensäften* // Flüss. . Obst. – 1972. –Bd. 38, №10. – s. 439-441;

[9] Benk E., Dittrich J. Zur *Beurteilung von Zitrussa'ften mit Hilfe des Prolingehaltes und des Quotienten Formolwert*. :Prolin// Dstch. Lebensmittel Rdsch. – 1976. – Bd. 72, №7. – s.239-243;

[10] Bergner- Lang B. *Neue Ergebnisse zur Bestimmung der Isocitronensaüre in Citrusfrüchten* // Dtsch. Lebensmittel Rdsch. – 1977. – 73. №7. – s. 211-216;

[11] Bonafaccia G., Stacchini P., Zanasi F. *Variazion del numero di formolo e del contenuto in aminoacidi liberi in succhi di arancia, durante vari processi di lavorazione industriale*. Nota2. // Riv. Soc. Ital. sci. alim. – 1983. – Vol. 12, №3.- p.185-190

[12] Boromiec Wieslaw, Golebiowski Tadeusz. *Rola niektorych uskaznikow jakosci w towaroznawczej ocenie pitnych sokow napojow owocowjch* // Zcsz. nauk. A E. Krakowie. – 1984. №89. - p. 53 – 64;

[13] Calabro G., Curro P., Lo Coco F. *Studio spettrofluorimetrico delle essenze agrumarie* // Essenze deriv. agrum. – 1977. - Vol. 47, №3. – p. 286-304;

[14] Coffin D.E. *Correlation of the Levels of Several Constituents of Commercial Orange Juice*. // J. Assoc. Offic. Anal. Chem. – 1968. – Vol. 51, №6. – p. 1199-1203;

[15] Coussin B.H., Samish Z. *Effects of Storage on the Formol and Chloramine- T Values of Processed Single-Strenght and Comminuted Orange Juice* // Food Technology. – 1966.- Vol. 20. – 115-116;

[16] E. Nijaradze, Z. megrelishvili, N. Mamulaishvili - "*Way of control of naturaless of tangerine juice*" G 01 N 33/00; № 59378.,2008;

[17] Hamed M.G.E., El-Wakeil Z. A., Foda. J.O. *Heikal Detection of accepted natural Juices in Carbonated beverages. Minerals and nitrogenous constituents of lemon juice concentrate beverage prepared therefrom* // Food Sci. – 1974. – Vol. 2, №1.- p. 45-57;

[18] Koch J., Hess D. Zum *Nachweis von vertälschten Orangensäften* //Dtsch. Lebensmittel-Rdsch. – 1971. – Bd. 67, №6. – S. 260-265;

[19] Licandro Kianvincenzo, Ragonese Carlo, Dugo Giacomo, Dugo Giovanni. *Sul contenuto di ione ammonio in gucchi industriali di arancia limone e mandarino* //Essenze derive. agrum. – 1983. – Vol. 53, №3. – P. 334-346;

[20] Lifshitz A., Heiger P.J. *Phosphorylated compounds in citrus juice* //Lebensm – Wiss. Technol. – 1985. Bd. 18, №1. – S. 43-46;

[21] Lifshitz A., Stepak J., Morton B. Broun. Fruit *and Fruit Products, Method for Testing the Purity of Israeli Citrus Juices* // J. of the AOAC. – 1974. – Vol. 57, №5. –p. 1169-1175;

[22] Morton B. Broun, Eli Cohen. *Discussion of Statistical Methods for Determining Purity of Citrus Juice.* //J. Assoc. Offic. Anal. Chem. – 1983. – Vol. 66, №3. – p. 781-788.

[23] Morton B. Broun, Eli Cohen. *Discussion of Statistical Methods for Determining Purity of Citrus Juice.* //J. Assoc. Offic. Anal. Chem. – 1983. – Vol. 66, №3. – p. 781-788.

[24] Neidman P. D. *Ein Beitrag zur quantiativen Bestimmung der freien Aminosäuren und des Ammoniaks in Orangensäften* //Dtsch. Lebensmittel-Rdsch. – 1976. Bd. 72, №4. – S. 110-126;

[25] Ooghe W. *Mogelijkheden van de aminozuuranalysator bij het opsporen van vermengingen er vervalsingen van sinaassap //* Voedingsmiddelentechnologie. -1980. – Bd. 13, № 15. – s. 11- 17;

[26] Ough C.S. *Rapid determination of Proline in Grapes and Wines* // J. Food Sci. – 1969. – Vol. 34. – p. 28-230;

[27] Petrus D.R., Attaway J.A. *Visible and ultraviolet absorption and fluorescence excitation and emission characteristics of Florida orange juice and orange pulp wash: detection of adulteration* //J. Assoc. Ofiic. Anal. Chem. – 1980. – Vol. 63, №6. – P. 1317-1331;

[28] Petrus D.R., Doughery M.H. *Spectral characteristics of Threl* Vol. 47, №3. – P.286-304;

[29] Petrus D.R., Fellers P.L., Anderson H.E. *orange juice adulteration: detection and quality effects of dilution, added orange pulpwash, turmeric and sorbate* // J. Food Sci. – 1984. – Vol. 49, №6. – P.1438-1443;

[30] Richard Jean- Paul Coursin Daniel. *Lemploi des methods statistiques multidimensionnelles: Une methode efficace de dissuasion contre les frandes economiques dans les jus d'agrumes*. // Jnd. alim. et. agr. -1982. – Vol. 99, №1-2. – p. 41-44;

[31] Royo Jranzo. R. *Methodos para la deteccion de frandes en los zumos citricos* // Rev. agroguim . y technolog. alim. – 1975.- Vol. 15,№2. – p. 162-166;

[32] Sandos M. Tanner H. *Ueber die Prolin Bestimmung nach OUGH in hellen und hochfarbigen Fruchtsäften und deren Konzentraten* // Schweizerische Zeitschrift für Obst. - und Weinbau. – 1975. – Bd. 3, №25. – s. 639-647;

[33] Sparenburg J. *Die Bestimmung der Formalzahl von Fruchtsäften //Die industrielle Obst – und gemuseverwertung.* – 1972. Bd. 57, №18. – 485-489;

[34] Vandercook C.E., Lee S.D., *Smolensky D.C. A rapid automated microbiological determination of orange juice authenticity* //J.Food Sci.- 1980.- Vol. 45, №5. – p. 1416-1418;

[35] Vandercook C.E., Mankey B.E., price R.L. *New Statistical Approach to Evalution of Lemon Juice* //J. Agr. Food. Chem. – 1973. – Vol. 21., №4. – p. 681-683.

[36] Vandercook C.E., Mankey B.E., price R.L. *New Statistical Approach to Evalution of Lemon Juice* //J. Agr. Food. Chem. – 1973. – Vol. 21., №4. – p. 681-683.

[37] Vandercook C.E., Navarro J.L. Smolensky D.C., Nelson D.B., Park J.L. *Statistical Evalution of data for Detecting Adulteration of California Navel Orange Juice.* // J. of Food Sci. – 1983. – Vol. 48. – P. 636-683.

[38] Vandercook C.E., Navarro J.L. Smolensky D.C., Nelson D.B., Park J.L. *Statistical Evalution of data for Detecting Adulteration of California Navel Orange Juice*. // J. of Food Sci. – 1983. – Vol. 48. – P. 636-683.

[39] Vandercook C.E., Smolensky D.C. *Easy method detects juice dilution*. // Food Prod. Develop. – 1979. Vol. 13, №1. – p. 60-61;

[40] Wallrauch S. *Aminosäuren- Kriterien für die Beurteilung von Fruchtsäften* // Flüss. Obst. – 1977. – Bd 44, №10.- s.386-391.91. Menziani E., Rossetti V., Garrone A. *Sugli aminoacidi liberi di succho naturali e comerciali di pompelmo*. // Boll, chim. Unione ital. lab. prov.- 1976. – Vol. 27, №11. – p.301-309;

[41] Wallrauch S. *Beitrag zur Erkennung manipulierter Formolzahlen bei Orangensäften* //Flüss. Obst. – 1974. – bd. 41, №10. – S. 414, 418, 420;

[42] Wallrauch S. *Mőglichkeiten zur Feststellung der Authentizitat von Fruchtsäften* // Voedingsmiddelenetechnologie. 1983.- Bd. 16, №24.- s. 30-35;

[43] Wallrauch S. *Prolinbestimmung in Fruchtsäften Bedeutung für die Beurteilung* //Flüss. Obst. – 1976, Bd. 43. – s.430-437;

[44] Wallrauch S., Greiner G. Bestimmung der D – *Isocitronensaure in Fruchtsäften und alkoholfreien Erfrischungsgetranken* // Flüss. Obst. – 1977. – Bd. 44, №6. – s. 241-245;

[45] Wallrauch S.*Über deu natürllichen Nitratgehalt von Orangensäften und seine Bedeutung fur deren Beurteilung* //Flüss. Obst. – 1971.-Bd. 38, №6. – s. 271-272;

[46] Wucherpfenning K., Franke J. *Beitrag zum Nachweis von verfalschten Produkten aus Orangensäften* //Dtsch. Lebensmittel-Rdsch. – 1985. – Bd. 61, №8. – S. 229-231.

[47] Нижарадзе Э.Ш., Хиникадзе Т. М. – *«Об одном способе определении натуральности мандаринового сока» Пиво и напитки*». 2008. №3.с.26-27;

[48] Э. Ш. Нижарадзе - „*Использование аминокислот для установления натуральности мандаринового сока*" „GEORGIAN ENGEENERING NEWS", №3, 2006.стр 285-287

[49] Э.Ш. Нижарадзе „Способ *контроля натуральности мандариновых соков*"- Патент №1793372 33/02 33/14. 8.10.92;