H.-J. Hofsommer

Definition of Orange and Orange Juice – Analytical Aspects*

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• Analysis • Citrus reticulata • Orange Juice • Polyphenolic Fingerprint • RSK-Values

During this IFU meeting there were many lectures about different orange varities, their classifications, economical and legal aspects. Especially the economical and legal aspects need an answer to the question of authenticity of a product. If no differences between the varieties can be detected objectively, the discussion about legal aspects is in our opinion theoretical.

Before starting this lecture about different analytical aspects, it has to be pointed out that it is a difficult work for the analyst to decide whether the orange juice is really an authentic juice of citrus sinensis or perhaps a blend of oranges and hybrids or even a mixture of other varieties of citrus like mandarine, grapefruits or similar fruits. No doubt, a possible answer is always based on the established knowledge due to a special question. A lot of work was done describing the characteristics for orange juice based on the traditional parameters and many publications are available. Therefore it is easy for an expert to see the differences. Pera can be easily be distinguished from Shamouti or California Navel from a Spanish Valencia.

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Other examples like different varieties from Italy, Morocco, North Brazil, etc are well established. Even peculiarities like the so-called Temporona, which is a third flowering Pera, can be recognized very easily. Of course, those traditional judgements, based on RSK-figures, have a certain limit by mixtures and a lot of experience is necessary for the right answers. It appears that even today – after 20 years experience – an expert may find unknown facts. This happens mainly if new varieties or hybrids are on the market or origins which were unimportant in the past become popular. It seems to be very easy for me to give a two hours lecture how those differences can be detected traditionally, but this could be boring. Anyhow, it has to be kept in mind that the traditional way is still a very important aspect today. The aim of the analytical work was and is always to find characteristic components.

A few years ago additions of grapefruit in orange juices were detected first. Today it is an established knowledge that naringin, which is a typical component of grapefruits, is not present in oranges. But also some other citrus varieties content

*) Lecture given on IFU workshop in Parma 1994.

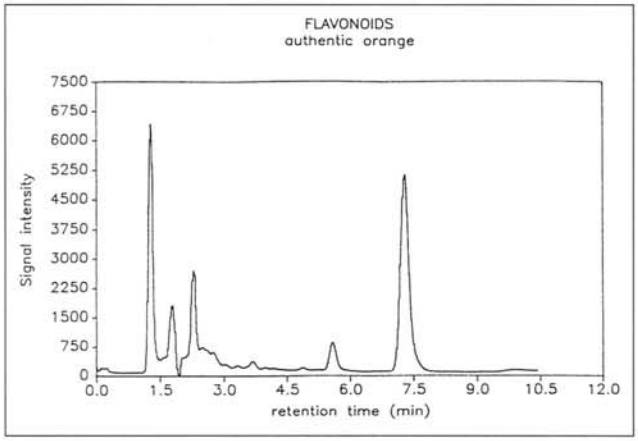

Fig. 1: Flavonoid chromatograms of different citrus varieties

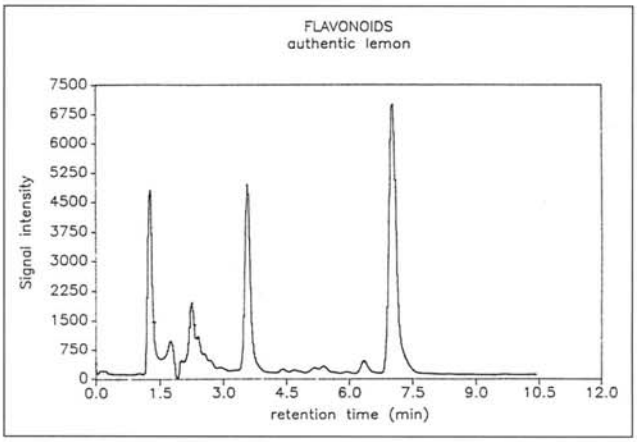

Fig. 2: Polyphenolic fingerprint

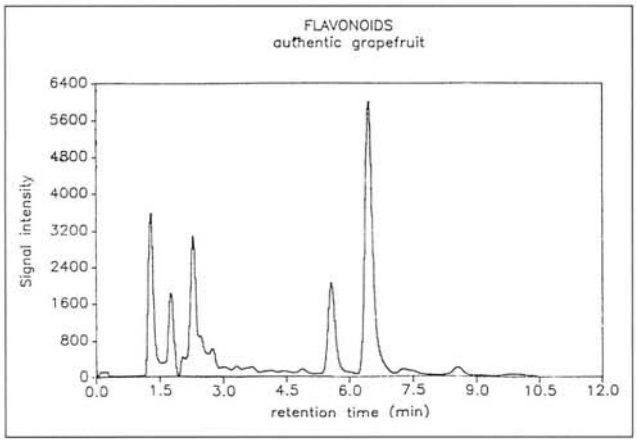

Fig. 3: Cryptoxanthin contents in different cultivars

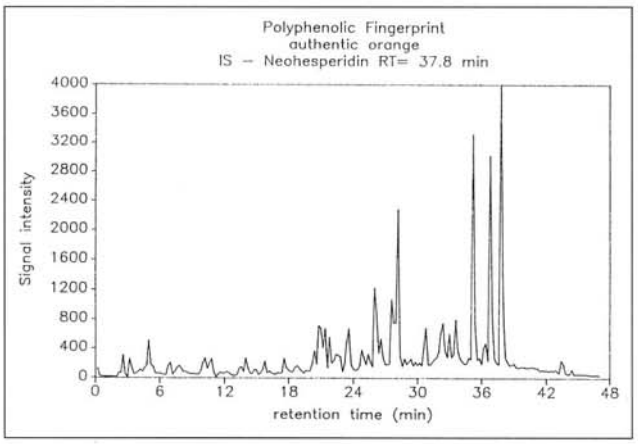

Fig. 4: Carotinoid distribution of mandarin type 1

naringin, for example sour orange, and this must be considered for a precise attestation. There is no need to start with old stories, but looking to the flavonoid fingerprint is – even today – one of the possiblities to find differences between citrus varities as it is shown in Fig. 1.

Not only the components hesperidine and naringine are important in this view. Others, like rutine, narirutine, neohesperidine, etc. and the ratios between the flavonoids get an important aspect. Since an official IFU method was established, the analytical knowledge is widespread today.

Higher sophisticated is the information based on a polyphenolic fingerprint as established by Procter & Gamble at end of the eighties. An example is shown in Fig. 2. Such a pattern includes much more components as the flavonoids already mentioned. It is a pity that – as far as we know – there was no real follow-up based on this method for establishing a wide database which could be helpful for characterization of citrus varieties. It has to be supposed that this interesting way was blocked due to the problems of a safe interpretation of such complex chromatograms. Today, where chromatography pattern recognition programs are available, it seems to be worth to focus again on this analytical aspect.

It is very clear, most problems about mixtures cannot be solved by performing a single analytical method, because normally a single component could not be recognized as typical for a special variety. The whole spectrum of citrus fruit components are normally present in all varities, but the concentration may differ. Even among the traditional RSK-analysis, several components may indicate a blend between sinensis and reticulata by their concentration. For example, it is well established that the cryptoxanthinester fraction in reticulata types has a higher percentage from the total carotinoids as sinensis ones. The limit of max. 15 % cryptoxanthinester has given a good indication for mixtures. Anyhow, some sinensis types like pigmented oranges sometimes show higher values and for Pera type the guide value is much too high. As mentioned, it might be wrong to take only one single parameter. An expert's judgement will always take into account other parameters like l-malic acid and the content of sucrose because reticulata types are generally high in sucrose and low in l-malic. Looking a little bit deeper into this subject of cryptoxanthin Fig. 3 demonstrates a more sophisticated information worked out from Prof. Rousseff (University of Florida – Department of Citrus) during his sabbatical studies at GfL this year. These results generally confirm the experience mentioned in comment of RSK.

As it is shown, three categories were established. The reason for deviding the cultivars of Mandarines in two groups is a significant difference between the Mandarine types analysed. Normally ß-cryptoxanthin usually results for 70 % or more of the total peak area (Fig. 4). In other samples of juices from Mandarin or Mandarin hybrids cryptoxanthin was not the major peak. In this set the major peak at 486 nm was zeaxanthin as shown in Fig. 5. To make it more clear it has to be mentioned that these chromatograms were established after saponification. To get a final conclusion about these facts it seems to

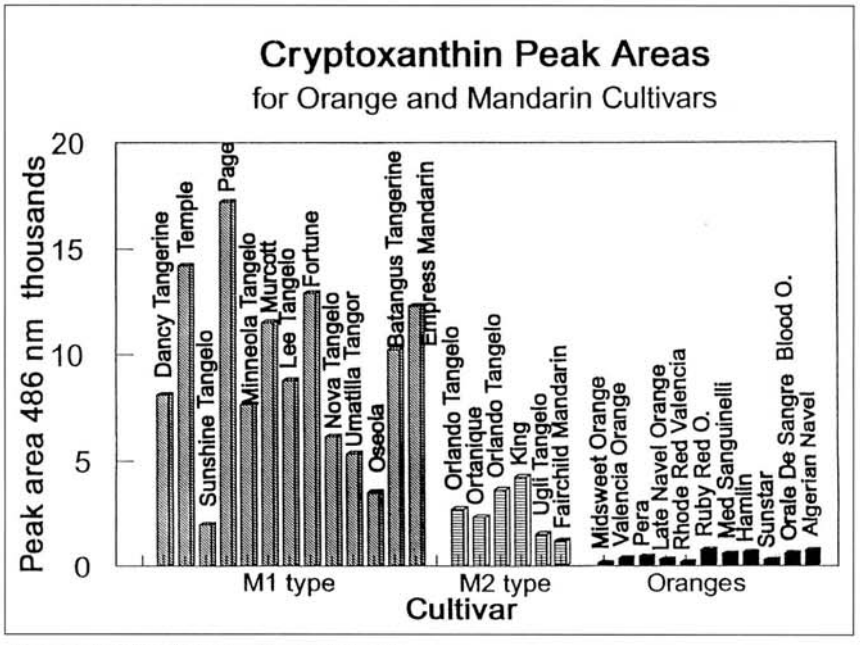

Fig. 5: Carotinoid distribution of mandarin type 2

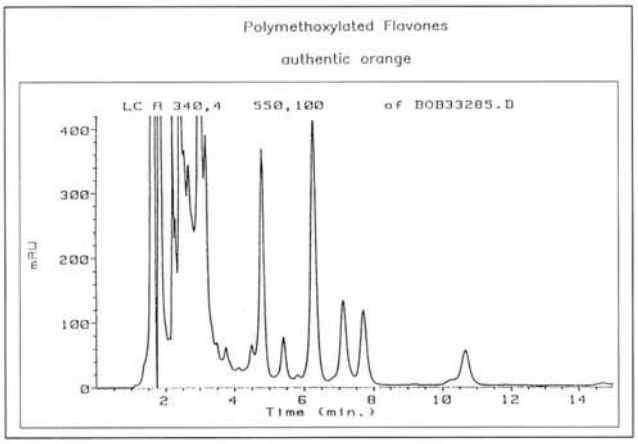

Fig. 6: PMF fingerprint

SOME IMPORTANT ANALYTICAL ASPECTS

- TRADITIONAL PARAMETERS (RSK)
- FLAVONOIDS
- POLYPHENOLS
- CAROTINOIDS
- POLYMETHOXYLATED FLAVONES
- AROMA COMPONENTS
- LIMONOIDS

Fig. 9: Analysis for the classification of citrus juices

be necessary to include the knowledge about the botanical origin of these samples into the consideration. Anyhow, these facts indicate some exciting differences.

More informations are available in the carotinoid pattern as already presented in the special lecture about carotinoid fingerprint analysis. Of course, the use of pattern recognition and a database including hundreds of authentic samples are necessary. Although satisfying results are performed with this analytical tool, we do not want to make it too important. A lot of possible influences are not quite well researched, especially weather conditions, stage of maturity, etc. It has to be mentioned that results coming from carotinoid pattern are only one part in the big puzzle of authenticity.

Another important method seems to be the determination of polymethoxylated flavones (PMF). This method can be performed simply in a routine way and the interpretation of the chromatograms basically shows no problems (Fig. 6). It seems to be easy to build up a database for these few components everywhere in the world. We did a lot of work during the last few years and know quite well the differences between the fruits. In citrus six main components are typical and their concentration show big differences caused by the varieties as shown in Fig. 7. This graph is based on an average concentration. Typical for reticulata is Tangeritin, but – and this is a pity – small amounts are found in sinensis varieties, too. Even if differences caused by various origins may appear, it can be concluded that the pattern is quite similar within the sinensis group as shown in Fig. 8. Additional to other different analytical aspects, the knowledge of the PMF pattern is very helpful for a correct classification of authenticity.

Speaking about analytical aspects according to the title of this workshop, nobody can ignore the sensorical evaluation. In this meeting there were lectures about the colour appearance in carotinoids and anthocyan pattern for the pigmented oranges. Also the taste of the product is most important. Besides, a sensorical panel which might be able to detect differences, analytical methods in the field of aroma components are useful for classification. This aspect includes not only the classic volatile components. The group of limonoids, e.g. limonin, is also very important. Those bitter tasting components are also typical for certain varieties and such a pattern might be helpful for characterization. It is not possible to intensify these sensorical aspects, because many different analytical procedures are established and influences during technology, origin, maturity, etc. are strong. Generally, this part of analytical work also results in a typical complex pattern respectively in the determination of single components which were choosen as typical. As far as we are informed, especially this part of analytical aspects was the main argument for classification of Ambersweet as an orange. Although everybody knows the botanical composition of this hybrid. The aroma components of such a juice are – up to our information – the same as for an orange juice.

Summarizing the analytical aspects which might be able to help to define orange and orange juice it is hard to give a satisfying answer. Mainly no single method is available to clearly detect whether a mixture of different varieties or hybrids were used for the final product orange juice. As a conclusion, Fig. 9 shows some important analytical aspects which may be helpful when used in combination to fulfill the requirements of a scientifically based classification of citrus juices.

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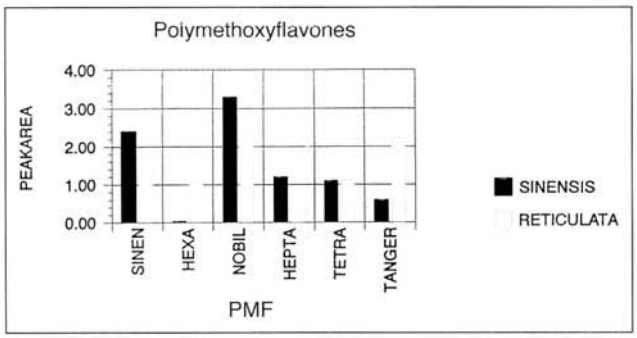

Fig. 7: PMF distribution of Citrus sinensis and Citrus reticulata

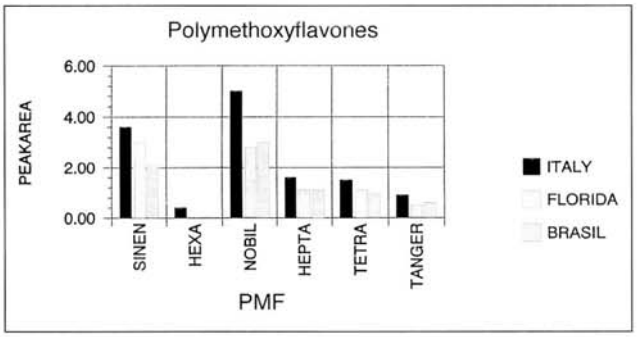

Fig. 8: Distribution of PMF of Citrus sinensis from different origins