

Discrimination of sweeteners based on the refractometric analysis

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Abstract. In the present work, the refractive characteristics of aqueous solutions of several sweeteners are investigated. These data in combination with ones from other sensors should find application for brief determination of sweeteners content in food and dynamic monitoring of food quality. The refractive indices of pure (distilled) water and aqueous solutions of several commonly used natural and artificial sweeteners (glucose, fructose, sucrose, lactose, sorbitol [E420], isomalt [E953], saccharin sodium [E950], cyclamate sodium and glycerol [E422]) with 10 wt.% concentration are accurately measured at 405 nm, 532 nm and 632.8 nm wavelengths. The measurements are carried out using three wavelength laser microrefractometer based on the total internal reflection method. The critical angle is determined by the disappearance of the diffraction orders from a metal grating. The experimental uncertainty is less than ± 0.0001 . The dispersion dependences of the refractive indices are obtained using the one-term Sellmeier model. Based on the obtained experimental data additional refractive and dispersion characteristics are calculated.

1. Introduction

As for all food additives, the sweeteners are regulated substances, which are a subject to safety evaluation prior to market authorization. Over the centuries various foods such as honey or sugar have been used to sweeten our food. Today we also have a range of new sweeteners, which provide alternatives to sugar. Natural sweeteners provide calories in the form of sugars. Some are found naturally in foods like fruit and milk and others are added to foods during preparation or processing, for example, high fructose corn syrup and others [1-3].

Artificial sweeteners provide zero or very low calories since the molecules are large and are partially indigestible. Most are usually much sweeter than sugar. The Food and Drug Administration (FDA) has approved the use of the only five of them. They are less expensive than most sweeteners and is stable under heating [4].

Therefore, the selective identification and sensitive identification and sensitive determination of different sweeteners are necessary to effectively perform food quality control. Several analytical techniques can feasibly be applied to the analysis of natural sugars and artificial sweeteners. High-performance liquid chromatography (HPLC) [5-9] coupled (or not) to mass spectrometry [10] is the most popular method for determining sweeteners, although this approach is relatively complicated for on-site food quality control applications. Furthermore, enzyme [11, 12] or enzyme-free sensors, such as



electrochemical sensors [13], fluorescent sensors [14], spectrometric sensors [15], colorimetric sensors [16] and diffraction resonance sensors [17] are relatively simple, but these methods are usually only used to determine a certain type of sweetener – they may lack sufficient selectivity to be able to identify various sweeteners in a food content.

The aim of the present paper is to make an analysis of the refractive indices of several commercially used natural and artificial sweeteners for its fast and precise detection and discrimination.

2. Materials and experiments

2.1. Materials

Glucose, sorbitol [E420], glycerol [E422], saccharin sodium [E950] purchased from Valerus, Bulgaria and sucrose, fructose product of Fillab, Bulgaria are used. Other sweeteners (cyclamate sodium and isomalt [953] are bought from the local market. All of them have been used without any characterization and modification. The aqueous solutions with concentration of 10 wt.% are made from chemically pure sweetener and a distilled water by stirring. For the sample preparation the used sweetener and the solvent are weighted with accuracy ± 0.0001 g by using an analytical balance.

2.2. The refractive index measurement

The refractive index values of the investigated samples are measured by the laser refractometer based on the method of the disappearing diffraction pattern for three different laser wavelengths – 405 nm, 532 nm and 632.8 nm respectively at a room temperature (22 °C). The principle scheme of the refractometric system is illustrated in [18]. The sample is placed between a measuring glass prism and a metal diffraction grating. When the laser light strikes the base of the prism at an angle smaller than the critical one, it penetrates through the sample, reaches the diffraction grating forming a diffraction pattern on a screen. The incident angle gradually changes via rotating stage, since at a critical angle φ_{cr} , total internal reflection is observed. As a result, the diffraction pattern disappears because the incident light cannot reach the diffraction grating. In this way the critical angle φ_{cr} is measured in air at a chosen wavelength. The refractive index was calculated by the following equation:

$$n = N \sin \left[A \pm \arcsin \left(\frac{\sin \varphi_{cr}}{N} \right) \right]. \quad (1)$$

The signs (+) and (–) correspond to clockwise and counter-clockwise measurement of φ_{cr} , respectively. In our case, the sign is (–). In equation (1) $A = 64.75^\circ$ is the reflecting angle of the prism, N is the refractive index of the prism.

The main source of experimental uncertainty is the used rotary stage with $\Delta\varphi = 1$ arcmin resolution. By using equation (1) the experimental uncertainty can be estimated as:

$$\Delta n = N \Delta\varphi_{cr} \cos \varphi_{cr} \quad (2)$$

In our case, since the obtained values of the critical angle are of the order of 25° , we have $\Delta n = \pm 1 \times 10^{-4}$ for the experimental uncertainty.

The optical properties of the materials are usually presented by their dispersion dependences. For the most optical materials, far from the fundamental absorption band, the dispersion dependence of their refractive index can be build using the Sellmeier dispersion equation, if they are non-magnetic [19].

The values of the coefficients s and λ_s - the so called the Sellmeier's coefficients, can be obtained using the following relation [19]:

$$n^2 - 1 = \frac{s\lambda^2}{\lambda^2 - \lambda_s^2}. \quad (3)$$

In this paper the values of Sellmeier's coefficients are obtained by non-linear fitting the set of experimentally determined values of the refractive index with the relation (3) using Wolfram Mathematica® software [20]. The confidence level is 0.95. By using the coefficients s and λ_s the

dispersion dependences of the refractive index are built, by the approximated values in the spectral range 400 nm – 800 nm.

3. Results and discussion

The investigated samples basically can be divided in five groups, depending on their chemical structure and origin as follow:

- monosaccharides (glucose and fructose),
- disaccharides (sucrose and lactose),
- alcohols (sorbitol and isomalt),
- artificial (saccharin sodium and cyclamate sodium),
- glycerol.

As the last sample for testing, we choose glycerol because it is not a typical sweetener, but has a sweet taste due to the large numbers of alcohol groups. It is sometimes added to food products because it retains moisture in them for longer time or to prevent the crystallization of the sucrose.

The refractive index values of the all samples are measured at three different wavelengths – 405 nm, 532 nm and 632.8 nm respectively at a room temperature (22 °C).

The measured values of the refractive indices and the Sellmeier's coefficients at used wavelengths are presented in table 1.

The constructed dispersion dependences are presented on figure 1.

Table 1. Refractive indices at the used laser wavelengths and obtained values of the Sellmeier's coefficients.

| | n (405 nm) ±0.0001 | n (532 nm) ±0.0001 | n (632.8 nm) ±0.0001 | s | λ_s |
|--------------|------------------------------|------------------------------|--------------------------------|----------|----------------------|
| Glucose | 1.3555 | 1.3471 | 1.3438 | 0.786 | 100.68 |
| Fructose | 1.3574 | 1.3488 | 1.3454 | 0.789 | 102.03 |
| Sucrose | 1.3561 | 1.3490 | 1.3462 | 0.795 | 93.19 |
| Lactose | 1.3567 | 1.3493 | 1.3464 | 0.795 | 94.47 |
| Sorbitol | 1.3573 | 1.3492 | 1.3460 | 0.792 | 99.04 |
| Isomalt | 1.3574 | 1.3493 | 1.3462 | 0.793 | 98.55 |
| Glycerol | 1.3530 | 1.3461 | 1.3434 | 0.788 | 91.98 |
| Saccharin-Na | 1.3600 | 1.3515 | 1.3482 | 0.797 | 100.80 |
| Cyclamate-Na | 1.3547 | 1.3474 | 1.3446 | 0.790 | 94.23 |

The measured values of the refractive indices are very close to each other at the used wavelengths (table 1). From figure 1 it can be seen that the dispersion curves are very close to each other and some of them intercross.

Since it is not possible to make a clear separation between investigated sweeteners based on the measurement of the refractive index at one wavelength or on the dispersion curves, the Abbe numbers (ν) for all samples are calculated using the simple relationship:

$$\nu = \frac{n_D - 1}{n_F - n_C}, \quad (4)$$

where n_D , n_F and n_C are the refractive indices of the sample at 589.3 nm (D line), 486.1 nm (F line) and 656.3 nm (C line), respectively.

The calculated values of Abbe numbers are presented in table 2.

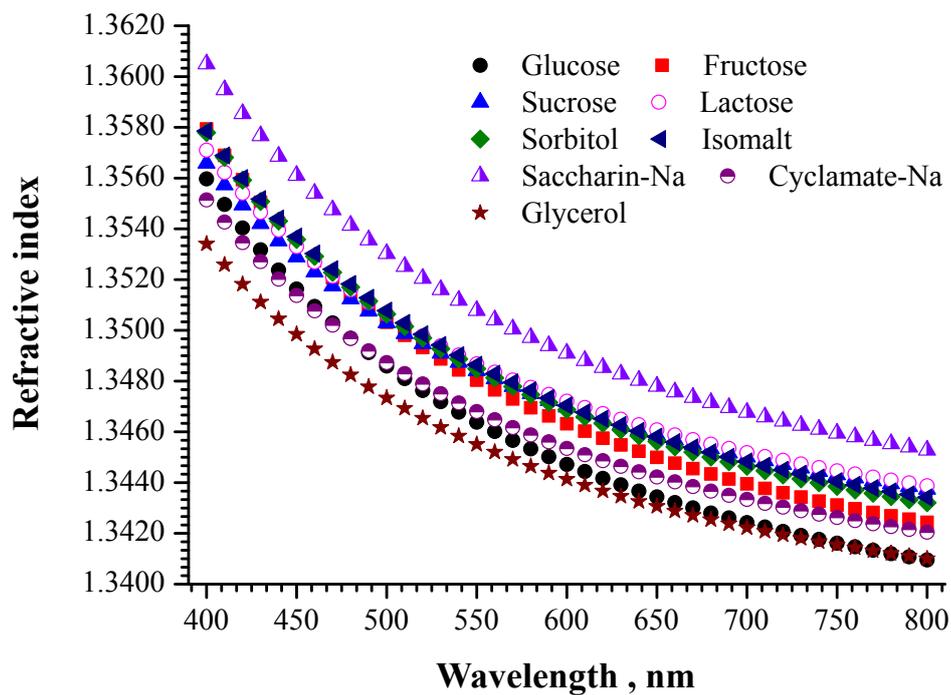


Figure 1. Dispersion dependences of the investigated sweeteners in the visible range.

On figure 2 a 2D mapping of the measured refractive indices at 405 nm versus the Abbe numbers is made. It is convenient to use the refractive index values of the short-wave region (405 nm) due to the strong dispersion. The dependencies at the other wavelengths, where the refractive index is measured, are similar but not so clearly visible.

Table 2. Calculated values of Abbe numbers for the investigated sweeteners.

| Sample | v |
|------------------|---------|
| Glucose | 57.0773 |
| Fructose | 55.5578 |
| Sucrose | 67.0350 |
| Lactose | 65.1742 |
| Sorbitol | 59.1058 |
| Isomalt | 59.1058 |
| Glycerol | 68.8057 |
| Saccharin sodium | 57.0214 |
| Cyclamate sodium | 65.4821 |

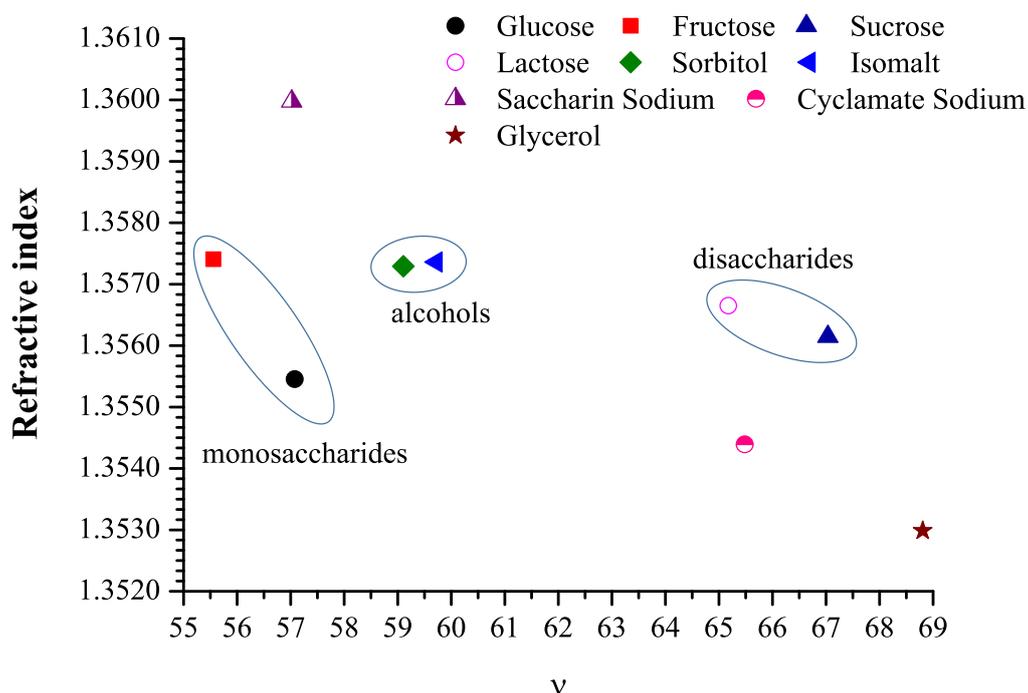


Figure 2. Measured refractive index for investigated samples at 405 nm versus the Abbe numbers.

The investigated sweeteners formed three groups. From figure 2 it can be seen that the investigated monosaccharides have refractive indices between 1.3550 and 1.3575 and Abbe numbers between 55 and 57. The alcohols have refractive index around 1.3575 and Abbe numbers between 59 and 60. The disaccharides have refractive index between 1.3560 and 1.3570 and Abbe numbers in the range 65-67. It was found that the most sensitive parameter for distinguishing natural sweeteners is the Abbe number at the small wavelengths of the visible range. For the artificial sweeteners, there is no differentiation in a separate group due to its distinct chemical composition and structure.

4. Conclusion

This work has made one first attempt to separate several sweeteners – monosaccharides, disaccharides, alcohols and artificial using experimental data from the refractometer measurements that have been carried out in an easy, fast and inexpensive way. The refractive index values are measured by the laser refractometer using the method of the disappearing diffraction pattern for three different wavelengths. The results showed that the refractive index values and dispersion dependences in the visible range are not suitable for discrimination of sweeteners. It was found that discrimination of natural and artificial sweeteners by the Abbe number is not possible. If we know that is a natural sweetener used, this method can be used for its determination.

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