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FOURIER TRANSFORMED INFRA RED SPECTROSCOPY IN BEEPRODUCTS ANALYSIS

SPECTROSCOPIA FTIR ÎN ANALIZA PRODUSELOR APICOLE

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FTIR spectroscopy is a very recent technique mainly used so far for classification of honeys of different geographical and botanical origin, on identification of honey and other food products adulteration. Some of the advantages of FTIR methodology are described in this article.
Keywords: FTIR spectroscopy, Beeproducts, qualitative analysis, authenticity

Introduction

Honey is defined in EEC 110/2001 as "the natural sweet substance produced by honeybees from the nectar of plants or from secretions of living parts of plants or excretions of plant sucking insects on the living parts of plants, which the bees collect, transform by combining with specific substances of their own, deposit, dehydrate, store, and leave in the honeycomb to ripen and mature". The demand for natural products is increasing while the production is in decline for a variety of socioeconomic factors (Kelly, 2006). Identification of adulteration is important for financial reasons, for consumer and producer protection.

Many different analytical techniques are employed in authenticity testing of honey. Until now, the botanical origin of honey was achieved only by global interpretation of sensory, pollen and physico-chemical analysis carried out by experts (Ruoff, 2006). These methods have a large range of error in interpretation of the results due to high degree of subjectivism.

The analytical methods employed nowadays, although are reported to be successful, are costly, time consuming and require considerable analytical skill. Besides, most of them destroy the samples under test (Tewari, 2004). The ideal qualitative and quantitative analysis methods of beeproducts would be fast and

inexpensive, require little sample preparation, allow for automated sampling and provide highly specific information related to nectar sources the honey is derived from. Infrared spectroscopic methods are fast (Tewari, 2005), require very little or no sample preparation, no harmful agents, allow fingerprinting of the overall composition of honey and show excellent repeatability. High sensitivity of FTIR allows identification and quantification of unknown compounds even in very low concentrations (Ruoff, 2006).

Researchers apply Fourier Transformed Infra Red (FTIR) Spectroscopy as a screening tool for identification and classification of honey from different floral sources. Honey samples were usually scanned in the region 600-4000cm^{-1} (Tewari, 2005). FTIR can be used in all three regions: near IR, mid-IR and far-IR, each of them having advantages and disadvantages.

Near-Infrared Spectroscopy (NIR)

NIR has recently become a rapid and well established technique for qualitative and quantitative analysis of foods (Tewari, 2005). It has been applied in different fields like diary products (milk, cheese), fruit juices, and honey analysis (determination of botanical and geographical origin, quality control and detection of adulteration). Many articles have studied and evaluated the potential of NIR for the determination of the botanical and geographical origin of honey (Ruoff, 2006, Tewari, 2005).

Accurate predictions were obtained for fructose, glucose, sucrose, maltose, water and ash contents as well as for the fructose/glucose and glucose/water ratios in honey samples from different crops (Kelly, 2006). Non-compositional characteristics of honey such as electrical conductivity, color and polarimetric properties have been successfully calibrated. NIR have not been considered adequate for analysis of minor components such as HMF, free and lactone acidity as well as pH value (Tewari, 2005).

Mid-Infrared Spectroscopy

MIR provides more specific and distinct absorption bands and thus more informations than NIR. Minor sugars present in concentrations lower than 2g/100g as well as praline, HMF content and invertase activity could not be determined (Tewari, 2005, Lichtenberg-Kraag, 2002).

The MIR spectrum of honey is dominated by sugar absorptions; the most significant features of the raw spectra are peaks at 8713, 9460, 9680nm approximately and shoulders centered around 9080, 9300 and 10180nm.

MIR gives valuable results regarding the botanical origin of honey especially when used together with statistical tools like Principal Component Analysis (PCA). In order to perform classification of honeys, the initial strategy applied so far to develop model of authentic honeys and evaluate the performance of this model on different authentic honeys plus all of adulterated samples (Ruoff, 2006).

Tewari, 2005 succeeded to achieve accuracy of honey classification near to 100% for clover (South Dakota), buckwheat (Missouri), basswood (New York),

wildflower (Pennsylvania), orange blossom (California), carrot (Louisiana) and alfalfa (California).

Attenuated Total Reflectance (ATR-MIR)

ATR-MIR spectra contain valuable informations on the botanical origin of honey and can be used for quantitative analysis of main components in honey. Experiments were performed by Tewary, 2005, Ruoff, 2006.

Other researchers who have studied the honey composition and detection of adulteration are mentioned in Table 1.

This type of absorption spectroscopy reflects the overall chemical composition of the honey samples studied. It offers a very promising approach for the authentication of the botanical origin of honey. Usually honey samples were classified by using statistical tools like: principal component analysis (PCA), partial least squares (PLS). Infra-red spectroscopic techniques give an additional and independent point of view on the topic of authentication of the botanical origin of honey. They may be advantageous to better characterize unifloral honeys that are not yet well defined by the traditional physical and chemical criteria. Unfortunately infrared spectroscopic methods do not allow a quantitative determination of hydroxymethylfurfural and enzyme activities, criteria particularly important for honey trade, i.e. for evaluation of storage and heat damage.

Conclusions

Infrared spectroscopy in both MIR and NIR region is emerging as a highly potential qualitative as well as quantitative analytical technique in a wide range of applied sciences. It's potential as a valuable workhorse for detection, determination, separation and structure elucidation of materials is well recognized. There is still lot of work to be done, to harmonize the techniques and selection of principal criteria to be used for a reproducible and reliable determination of the botanical origin of honey. FTIR seems to be rapid, non-destructive, highly sensitive and accurate quantitative analysis of honey.

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Table 1. Bibliographical data regarding the FTIR determinations performed on honey compared with traditional methods.

Honey type	Botanical origin	Traditional determinations	FTIR	Validation	Reference
Monofloral	Rape, lime tree, acacia, heather, cornflower, clover, sunflower,	Moisture, invertase, sugars, pH, electrical conductivity, free acidity, organoleptic analysis, pollen analysis	Midinfrared spectra for botanical origin of honey sample.	Blends of monofloral and multifloral honeys	Etzold, 2007
Honeydew					
Not specified	580 honeys	Refractometry	Detection of adulteration	No	Kelly, 2006
Not specified	580 honeys	Refractometry	Detection of adulteration	Yes	Kelly, 2004
Monofloral	350 samples (Clover, buckwheat, basswood, wildflower, orange blossom, carrot)	No, only modern: GS, z-Nose, Discriminant analysis (PCA)	NIR and MID for determination of botanical origin	Yes	Tewari, 2005
Monofloral	50 different floral honeys		Glucose, fructose, Sucrose, Maltose	Yes (HPLC)	Tewari, 2004
Monofloral	Clover, Orange Blossom, Buckwheat	No	NIR Detection of adulteration with beet inverted sugar.	No	Sivakesava, 2001
Monofloral	Acacia, alpine rose, chestnut,m dandelion, heather, lime, rape	Chemical, pollen, sensory analysis	FT-MIR with ATR for determination of botanical origin	No	Ruoff, 2006
Honeydew	Fir, Metcalfa, Oak,	Chemical, pollen, sensory analysis	FT-MIR with ATR for determination of botanical origin	No	Ruoff, 2006
Polifloral	411 samples	Chemical, pollen, sensory analysis	FT-MIR with ATR for determination of botanical origin	No	Ruoff, 2006