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NEW TENDENCIES REGARDING MOLECULAR ABSORBTION SPECTROPHOTOMETERS WITH APPLICATIONS IN FOOD PRODUCTS CONTROL

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Abstract

The paper presents new tendencies and devices from the field of molecular absorbtion spectrophotometry with special applications in raw materials and finished food products control. The diode arrays and spectrophotometer- proof sticks are presented. Besides a series of specific advantages, all these devices have in common the fact that they allow real time suit of concentration and automatic control and adjustment of products transforming processes in industrial system.

General considerations

Productivity and quality problems in foods industry impose higher and higher demands to methods and devices used at controlling raw materials, inter-phase check and finished products. These demands may be satisfied only by using the latter-day achievement from the instrumental analysis field, and referring to spectrophotometry these achievements must have as common denominator the following:

- real time qualitative and quantitative analysis
- high spectral resolution
- relatively simple devices
- low cost
- if applicable, medium qualified service staff (*This specification refers to device working directly in productive plants*)

These demands are carried on by a series of latter-day achievements such as: Diode arrays, and photometer proof sticks.

New Tendencies Regarding Absorbtion Spectrophotometers

*Diode Arrays Spectrophotometers***.** The use of diode detectors is the most important achievement in the spectrophotometry field (Hollas

1995, Schmidt 2005). This type of detector allows UV-VIS-NIR spectrum taking over, meanwhile the in time-sequential scanning of all wavelengths is not necessary. The advantages are the due time data reading and transmission to automatic pursue and adjustment systems of concentrations and parameters with special applications in food processes. The most important application in food analytical chemistry is the use of UV-VIS-NIR diode array spectroscope as analyzer in HPLC chromatography (Matter, 1995). At low concentrations in trace field, the component to be followed often turns out the capillary column in a range of time when the spectrum cyclical scanning in the case of classical spectroscopes is at wavelengths wherein the respective species does not display absorption.

In this situation, the spectroscopic analyzer does not sense the presence of the respective species in mixture. It is also possible for the respective species to be detected at the beginning or end of chromatographic column exit by wavelengths where the species has maximum absorption. In this case the concentration indication/point is lower than the real one. It must be shown that one of the basic applications for this type of spectrophotometer analyzer is the analysis of mycotoxins from raw materials and food products. The figure 1 shows the optical scheme of a UV-VIS diode array. It is evident that this spectroscope has no mechanical or electromechanical moving element like the classical scanning ones. The second observation is that the whole spectrum given by the diffraction grating (5) gets at the same time on the diode array detector (6). The number of diode arrays/detector is at present 512, 1024, 2048 depending on its construction type, with wavelength resolutions greatly less than a nanometer (Robinson, 2005). Such resolutions can not be actually obtained by in time-scanning mono-chromatograms. The diode array detector has cut the way for spectrophotometric wells, but above all, this detector is a chip of small dimensions with a 25- mm length quartz window and it is already tending to the price of common electronic chip.

Such resolutions can not be actually obtained by scanning mono-chromatograms in time. Diode array detector has also opened the way for spectrophotometric wells, but above all, this detector is a chip of small dimensions equipped with a 25 mm quartz window and costs already as a common electronic chip, putting out of concurrence the

classical spectroscopic solutions equipped with slow and expensive moving scanning mono-chromators.

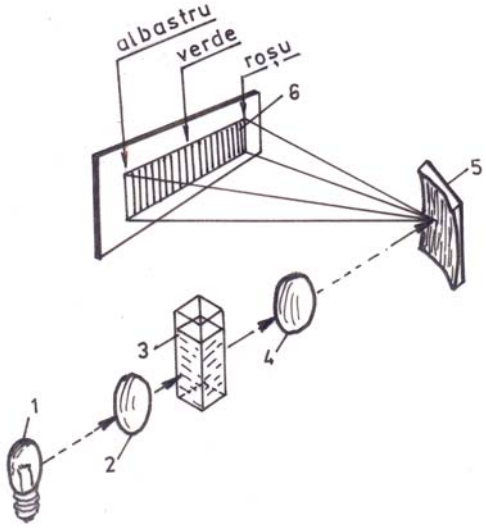


Fig.1. Optical Scheme of UV-VIS Diode Array Detector
1.-Source of polychromatic radiation, 2,4- groups of lens, 3. solution to be analyzed, 5. diffraction grating, 6.diode array detector

Spectrophotometric and Photometric Proof Sticks: The proof sticks used at determining qualitatively and quantitatively get greater extension due to the following reasons:

- allow real time and on-line data acquisition and distance-transmission
- measurement can be carried out in hardly accessible areas
- does not require specialized staff
- number of control points depends only on number of wells
- have a lower price than that of spectrophotometers

A spectrophotometric or photometric proof stick is an autonomous opto-electronic entity by the help of which measurement of composition or concentration in situ can be made, without extracting solution samples, the proof stick being emerged into the medium to be analyzed. There are manual proof sticks operated by man or energetically autonomous ones, usually floating, which can achieve the

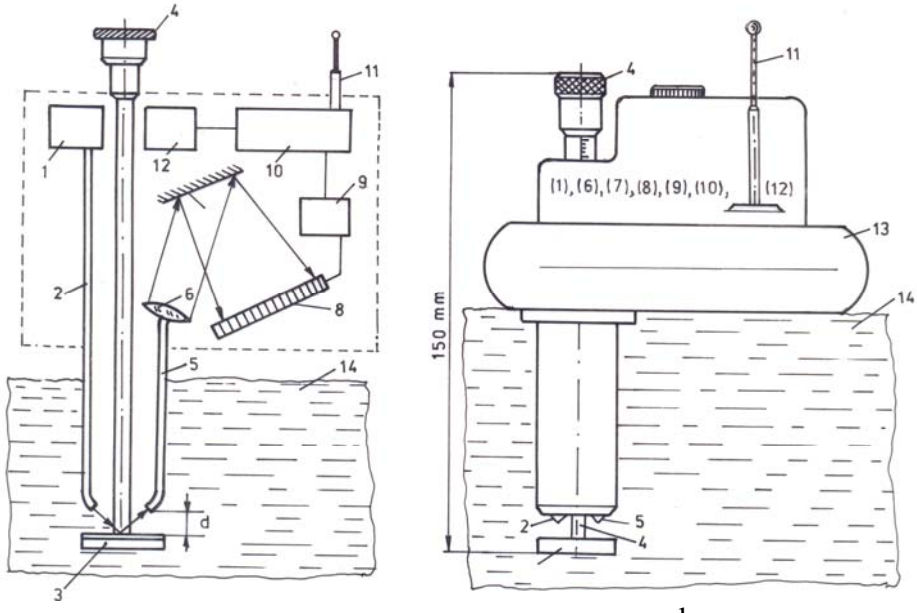
data distance-transmission by radio to distance of hundreds of meters. Data reception and processing is made in a centralized way by special peripheries and by a specialized soft computer. Mention must be made that proof sticks can be used both in photometric and turbidimeter regime, the latter application being used to determine the concentrations of muddy solutions (water, beer, spirits, wine, juices). The following factors have contributed significantly to promote and achieve proof sticks:

- industrial demand, especially food industry
- use of optical fibres as opto-conductor element
- appearance of detector diode array
- achievement of performing and cheaper chips for data distance-transmission.

The team research of Instrumental Analysis from the Food Engineering Faculty of Suceava has been focusing for many years on problems within the spectrophotometry field, including the achievement of an autonomous floating spectrophotometric proof stick intended for qualitative and quantitative determinations in the UV-VIS-NIR field (Gutt 2005, Gutt 2006). The well made by our team is a data distance-transmission by radio proof stick equipped with detector diode array. It can be used to determine composition and concentration in clear food stuffs (alcohol, beer, wine, juices) in UV-VIS-NIR field as well as suspension concentrations in solutions (drinking water, beer, thick new wine, pulp juice, etc). The proof stick principle scheme is shown in figure 2. The proof stick is intended to control open or closed large food recipients (without overpressure) and is equipped with a stainless steel float. The float shape and the proof stick weight center situated beneath the floating line make the proof stick return to its initial vertical position even if for different reasons it happens to be overturned.

The way of functioning is quite simple: the light radiation transmitted by the source (1) through optical fibre (2) goes through the solution to be analyzed on the distance (d) and it is reflected by plane mirror (3) through optical fibre (5) on lens (6) which reflects it on the diffraction grating (7). The UV-VIS-NIR spectrum falls to the diode array detector (8). After having amplified and digitized the signals in electronics (9), these ones are modulated into frequency and

transmitted by radio-emission electronics (10) to the radio-receiving electronics which lies next to the data processing central unit. This electronics can take over concomitantly and process data in real time starting with dozens of proof sticks of the types that have been already described. At the basis of qualitative analysis there is the spectrum of bands given by the photodiode array of 1 nm resolution.



a b

Fig. 2a,b. Principle scheme of autonomous spectrophotometric proof stick with data distance-transmission developed at University of Suceava.
1- radiation source, 2- optical fibre for incident beam, 3- plane mirror for radiation reflection, 4- micro-metric screw rod for layer thickness adjustment, 5- optical fibre for reflected beam, 6- colimator lens, 7 diffraction grating, 8- diode array detector, 9- amplifying and digitizing electronics, 10- radio-emission electronics, 11- emission antenna, 12- electrical accumulator, 13-float, 14-solution to be analyzed

At the basis of the quantitative analysis there is Lambert-Beer law. When the concentration is expressed in mol/l and the layer thickness in cm and the absorption measurement of mono-chromatic radiation is made, Lambert-Beer's law becomes:

$$A = \varepsilon \cdot b \cdot c \qquad (1)$$

Where: A- absorption (extinction) of molecular analyzed species [dimensionless]
ε- absorption molar coefficient [$1.mol^{-1}.cm^{-1}$]
b- thickness of the analyzed liquid layer [cm]
c- concentration of molecular species [mol/l]

Having in view that thickness of the analyzed liquid layer is once passed through by the incident beam and once by the reflected beam, at the measurements made by spectrophotometric proof stick, the value of layer thickness (b) is given by the double of the distance (d) between optical fibres (2), (5) and the mirror (3): b = 2d, and Lambert-Beer's law becomes:

$$A = 2 \cdot \varepsilon \cdot d \cdot c \qquad (2)$$

From the Lambert- Beer's law expression one can determine concentration (c) depending on absorption (A) on condition that the other two terms are constant. As for the concentration determining one should appeal to the method of concentration standard by comparing the solution absorption (extinction) of known concentration of the substance to be analyzed with the solution absorption of unknown concentration of the substance.

It is evident that at the same substance, the coefficients of molar absorption are identical, and the layer thickness of the solution of unknown concentration should have the same concentration as the one of known concentration, fact that implies the proof stick emerging into the solution of known concentration, followed by electronic memorizing of absorption value. Any further value of the absorption measured by the proof stick in liquid medium is transformed by rule of three into concentration values dealing with Lambert- Beer's law.

This method of calculation is possible only when Lambert- Beer's law is valid, namely in the linear field of dependence between concentration and absorption. It is known that the linear field is specific to small concentrations only between 0, 01-0, 02 mol/l. In the case when this dependence is non-linear there appear errors of determining. The higher they are, the higher deviation from linearity is. In this case it is recommended to draw a calibrating graphic with known concentrations. At classical photometers the calibrating graphic has two functions: on one hand to indicate the limit of Lambert- Beer's

law (Hesse 2005, Gutt 2006) applicability (the area where from non-linearity starts), on the other hand by extrapolation of the measured transmission which allows to determine unknown concentrations. At modern micro-processor-equipped photometers, the pairs of values absorption-concentration with which the calibrating plot is being carried out, are memorized, extrapolation being achieved automatically, the device displaying numerically the concentration value. Within the measurement-proof stick system, it is difficult to determine concentration by extrapolation on the calibrating graphic, the latter one being used only to determine the beginning of non-linearity. If the solution concentration overpasses the linear area at classical photometers one should appeal to known dilution till it gets into the linear dependence field. When measurement is made by proof sticks, real concentrations that can not be diluted are determined.

Therefore another parameter of Lambert- Beer's law must be acted upon which may be varied, this parameter is the layer thickness (d) of the solution to be analyzed (molar absorption coefficient (ε) is a constant specific to the analyzed molecular species). The distance (d) between optical fibres (2), (5) and the mirror (3) is at the same time equal to thickness of the analyzed liquid layer and may be varied by moving the fixing rod (4) of the mirror (3) by the help of a micro-metric screw until the layer decreases, thus being suitable for linear field concentration.

Conclusions

Molecular absorption spectroscopy in UV-VIS-NIR field is greatly marked by new methods such as: diode array spectroscopy and proof sticks- spectroscopy. All these techniques have basic applications in Food Analytical Chemistry and have in common the high speed of spectra achievement, giving the possibility to measure quantitatively and qualitatively in due time, to pursue on-line regime of composition and data automatic distance- transmission and processing, optimum control of manufacturing processes.

References

Geckeler, K., Eckstein, H. (1998). *Bioanalytische und biochemische Labormethoden*, Vieweg Verlag , Braunschweig

Gutt, G., Gutt, S. (2006). Sondă spectroscopică, propunere invenție 2006, *Oficiul de Stat pentru Invenţii şi Mărci Bucureşti*

Gutt, S. Gutt, G. (2005). Fotometria moleculară de absorbție metodă de analiză instrumentală în domeniul chimiei alimentare, *Analele Universității Suceava, secțiunea Chimie Alimentară*, nr 2, 14-20

Hollas, M. (1995). *Moderne Methoden in der Spektroskopie*, Vieweg Verlag , Braunschweig

Hesse, M., Meier, H. (2005). *Spektroskopische Methoden in der organischen Chemie*, Ed. 7-a, Thieme Verlag Stuttgart

Matter, L. (1995). *Lebensmittel und Umweltanalytik mit der Spektroskopie*, Wieley/VCH Verlag Weinheim

Robinson, J., Skelly, E. (2005). *Undergraduatet Instrumental Analysis,* Sixt Edition, Marcel Dekker, New York

Schmidt, W. (2005). *Optical Spectroscopy in Chemistry and Life Sciences*, Wieley/VCH Verlag Weinheim