Achievements in the Field of Spectroscopy: A Review

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Abstract: With recent advances in sensitive array detectors, fiber optic wave guides, high speed electronics and powerful softwares, many new generations of spectrometers have been developed. Microspectrometers, miniature spectrometers, portable spectrometers, or Fiber Optic Spectrometers are some of the names typically given to the class small spectrometers that are derived from simple, fixed optics, and low cost detector arrays. This class of instrument has been available for over 18 years, gaining industry acceptance with each year. From a very basic optical platform to sophisticated instrumentation for scientific investigation and process control, this class of instrument has evolved substantially since its introduction to the market. On board processing and memory have enabled the instruments to become fully automated, stand alone sensors communicating with their environment via analog, digital, USB and even wireless protocols [1].

Keywords: Array detectors, miniature fiber optic spectrometer, devices, sensors, portable spectrometers.

Rezumat: Odată cu progresul detectoarelor șir de fotodiode, al aparatelor electronice de mare viteză și al softurilor, s-au dezvoltat noi generații de spectrometrii. Microspectrometre, spectrometre miniaturale, spectrometre portabile sau spectrometre cu fibră optică sunt câteva din numele date de obicei, clasei mici de spectrometre care sunt derive de la sisteme optice simple, fixe și detectoare arrays cu un cost redus. Această clasă de instrumente este disponibilă de peste 18 de ani câștigând acceptarea industrii în fiecare an. Această gamă de spectrometre a evoluat considerabil de la introducerea sa pe piață, de la sisteme optice de bază la instrumente sofisticate pentru cercetările științifice și pentru controlul proceselor. Memorarea și prelucrarea „on board” au permis acestor siteme să devină complet automatizate realizându-se senzori spectrometrii autonome care transmit date prin semnale analogice, digitale, USB sau wireless [1].

Cuvinte cheie: Detector șir de fotodiode, spectrometru miniatural cu fibră optică, sonde, senzori, spectrometre portabile.

1. Introduction

Spectrometry has long been used for measuring chemical compositions and purity of materials in industrial, medical and environmental applications by detecting material dependent absorption of wavelength.

A spectrometer is a spectroscopic that has some sort of meter attached that can measure the amount of light (number of photons) at specific wavelengths. Thus, it is designed to provide a numerical measure of the amount of light emitted or absorbed at a particular wavelength. It is constructed so that the wavelength can be varied by the operator and the amount of radiation absorbed or transmitted by the sample determined for each wavelength.

Traditional laboratory optical spectrometers are tabletop-sized instruments that deliver very high performance. Current-generation industrial spectroscopic analyzers [2] are largely derived from this laboratory spectrometer technology, and they are typically housed in an environmentally controlled “shelter”, with lengthy fiber-optic runs to the actual points of measurement. While currently available diode-array and other miniature spectrometers [3] may seem like a plausible alternative, creating devices by merely shrinking existing technology, or employing linear array detectors has compromised range, resolution, signal-to-noise, and performance.

2. Traditional UV-VIS spectrometers with monochromator

Conventional UV-Visible spectrometers are composed of seven basic parts: the light source,
lens, a monochromator, the sample holder, detector, amplifier and a readout unit. Figure 1 is a schematic representation of a single beam UV-VIS spectrometer with a monochromator. The most commonly used light sources produce a continuous spectrum of radiation. As the Beer-Lambert Law does not hold for multiple wavelengths, a monochromator is used to select a single wavelength of light. There are several different methods that a monochromator can operate. One is to use a prism, and the other is to use diffraction grating [4].

The light leaving the monochromator is directed through the sample cell which contains the solution to be analyzed. A detector is used to determine the intensity of the radiation passing through the sample [5].

![Fig. 1. Schematic representation of a single beam UV-VIS spectrometer.](image)

Traditional spectrometers however, are table-top instruments. They are generally too large, and too costly to be ported outside of lab environments [6].

### 3. Spectrometer with array detector

These new spectrometers use detector arrays to replace the photomultipliers and avalanche photodiodes used in conventional spectrometers. The overwhelming benefits of array detectors are simultaneous and multi wavelength data acquisition. On the other hand, the use of fiber optics as light guidance allows a great modularity and flexibility in setting up an optical measurement system [7]. Figure 2 above presents the optical scheme of a spectrophotometer UV-VIS with array detector.

![Fig. 2. Schematic representation of UV-VIS spectrometer with array detector: 1 - light to be analyzed, 2, 4 - objective lens, 3 - sample cuvette, 5 - diffraction grating, 6 - array detector.](image)

It is especially noticed that this spectrometer has no mechanical or electromechanical moving element like classical scanning spectrosopes. In this type of photometer the light is divided in individual wavelengths only after passing through the tank. For each individual wanted wavelength there is an individual photodiode as detector of the absorbed light intensity. A second opinion is that the entire spectrum given by the diffraction grating (5) falls in the same time on the lane detector of photodiodes (6). The number of photodiodes/detector is nowadays of 512, 1024, 2048 taking into consideration its constructive type, with wave length resolutions much under the nanometer. Similar resolutions are practically impossible to reach with scanning monochromators in time.

The array generates an output that can be used to reconstruct the intensity of light striking each of the elements in the array. This output can be sent to a monitor or a printer for display. The output is instantaneous across the spectrum. No longer is it necessary to "scan" back and forth across the spectrum to identify light intensity at individual wavelengths.

### 3.1. Miniature fiber optic spectrometer

These are quick and easy-to-use instruments for generating VIS –NIR region spectra from any light source. The spectrophotometer (mirrors, grating, slit, and detector) is housed in an optical bench that’s small enough to fit into the palm of your hand.

The spectrometer accepts light energy transmitted through an optical fiber or free spaced and disperses it via the fixed grating across the linear array detector that is designed to provide output readings at 3648 evenly-spaced locations in the wavelength range of choice. The output from the detector is then fed into the computer via USB to software, processed, and displayed on the monitor as "counts" per millisecond.
This type of miniature spectrometers comes without a light source or sample system, allowing you the freedom to choose the accessories that best fit your setup, but if you want there are spectrometers that are equipped with a direct-attach light source and sample holder. The light source includes a led-boosted tungsten source and a sample holder for cuvettes that connects to the front of the spectrometer.

The advantage of their modular design is that when you purchase a miniature fiber optic spectrometer you can also choose a complete line of spectroscopic accessories. Most accessories have SMA 905 connectors for application flexibility. Changing the sampling system is easy as unscrewing a connector and adding new components or accessories, such as spectrometer direct-attach accessories, and additional light sources, sampling holders, filter holders, flow cells, fiber optic probes and sensors (for real-time, in situ analyte monitoring), collimating lenses, attenuators, diffuse reflectance standards, integrating spheres and a variety of optical fibers [8].

3.2. Devices

The array detectors have opened the way also to the spectrometric devices. The spectrometric devices are miniature devices that are directly introduced in the researched environment without the need to sample. Nowadays, the spectrometric devices are used both in portable systems in the sense that they are manually introduced in the sample to be analyzed or they are autonomous optoelectronic entities with online sending of the composition and concentration of a liquid mix.

A manual spectrophotometer device has a construction relatively simple. It is actually a miniature spectrophotometer in which the tank is replaced with a mirror reflection system of the light fascicle.

In autonomous devices that use wireless data tele-transmission systems, devices actually floating in closed or opened tanks that contain the product to be analyzed. The autonomous devices for quality and quantity determination become more and more common because: allow the acquisition and tele-transmission of data in real time and on line, measurements can be performed in areas with difficult access and their cost price is much lower than the spectrophotometers.

Spectrometric devices perform data tele-transmission through radio (active RFID system) at hundreds of meters distance. Reception and transforming of data is centralized through special peripheral devices and a specialized soft computer. One must add that spectrometric devices can be used in fotometric regime as well as in turbidimetric one, the last application being used to determine muddy solutions (water, beer, alcoholic drinks, wine, juice).

The use of optical fibers makes possible the transfer of the measurement process directly to process by using special measurement spectrometric devices from which the spectral information is sent through optical fiber to the analysis system. The advantages of using coupling optical spectrometric devices are: performing measurements directly in the process at high pressure and temperature, complete elimination of manual extraction and preparing of samples in order to get photo metered, data acquisition regarding the evolution of the process’s components composition and concentration is continuous and in real time and the possibility of high speed acquisition of complete spectres in case of chemical products with very high reaction speed.

4. Fourier transform spectrometer

A Fourier transform spectrometer is an adaption of the Michelson interferometer. A collimated beam from a light source is divided into two by a beamsplitter and sent to two mirrors. These mirrors reflect the beams back along the same paths to the beamsplitter, where they interfere. Figure 3 is a schematic representation of a FTS [9]. The signal recorded at the output depends on the wavelength of the light and the optical path difference between the beamsplitter and each of the two mirrors. If the optical path difference between the two beams is zero or a multiple of the wavelength of the light then the output will be bright, but if the optical path difference is an odd multiple of half the wavelength of the light then the output will be dark.

In the Fourier transform spectrometer, one of the mirrors is scanned in the direction parallel to the light beam. This changes the path difference between the two arms of the interferometer, hence the output alternates between bright and dark fringes. If the light source is monochromatic, then the signal recorded at the output will be modulated by a cosine wave; if it is not monochromatic then the output signal will be the Fourier transform of the spectrum of the input beam. The spectrum can then be recovered by performing a Fourier transform of the output signal [10].
This field of spectroscopy has been dominated by Fourier transform spectroscopy for many years because of several advantages over diffraction based optical designs. Fourier transform spectroscopy has greater optical efficiency, increased speed, increased sensitivity, and reduced maintenance. The precise placement, alignment, and control of miniature optical components on MOEMS structures allows the extension of Fourier transform spectroscopic techniques that are dominant in infrared ("IR") with the capability of real-time detection. A new class of Miniature Fourier Transform Spectrometer, at low cost has been developed.

5. Fluorescence Spectrometer

The fluorescence spectrometer is a complex instrument comprising (in its simplest form) a broad band light source, a monochromator, a sample cell, an appropriate grating, a diode array sensor and associated electronics. Light from the source passes through the monochromator and the excitation light wave length is selected. The excitation light is focused onto the sample contained in a suitable cell and the fluorescent light is focused onto the grating and thence onto a diode array sensor. The monochromator is programmable and so either the fluorescence spectrum of the solute at a fixed excitation wavelength can be obtained or an emission spectra obtained at a fixed fluorescence wavelength can be recorded. Figure 4. is a schematic representation of a fluorescence spectrometer [11].

A miniature fiber optic spectrometer for fluorescence offer high performance at low cost, in a convenient, modular package. Optical performance will vary according to a number of factors, including the groove density of the grating and the size of the entrance optic as well as the application itself [12].

Fluorescence spectroscopy is an important investigational tool in many areas of analytical science, due to its extremely high sensitivity and selectivity.

6. Raman spectroscopy

For many decades Raman spectroscopy has not been considered an useful analytical tool because of the very low efficiency of “normal” Raman scattering [13]. Therefore, to record conventional Raman spectra, analytical concentrations greater than 0.01M are usually required. Moreover, Raman spectrometers constructed in the previous decades were expensive and were not suitable for onsite analysis. Both these limitations of Raman spectroscopy have been, however, overcome. By utilizing special resonators constructed from metal nano-clusters the Raman scattering crosssections can be significantly increased e.g. to $2 \times 10^{-14}$ cm$^2$ per molecule [14], making possible observation of Raman spectra even of a single molecule [14–16]. Raman spectrometers have significantly profited from technical development and now it is possible to construct low-cost, battery-powered, portable Raman spectrometers, which have many of the spectral capabilities of laboratory-based systems [17]. Raman scattering: When monochromatic radiation of frequency $\nu_0$ is incident on a sample, some of the radiation is scattered. In the scattered radiation, in addition to radiation with the same frequency as the incident radiation (elastically scattered radiation-Rayleigh radiation), radiation of different frequencies (inelastically scattered radiation-Raman radiation) is also observed. The basic idea of the inelastic scattering may be described as follows: the interaction of the photon...
of energy $h\nu_0$ with the molecule may lead to the annihilation (virtual absorption) of the initial photon and simultaneous creation of a new photon of energy $\hbar (\nu_0 - \nu_n)$, accompanied by the transition of the molecule on which scattering occurs, to a state with energy higher by $h\nu M$ (usually an excited vibrational state). When the molecule is initially in the excited vibrational state, it is also possible to observe scattering that leads to the annihilation of the initial photon of energy $h\nu_0$ and creation of a new photon of energy $\hbar (\nu_0 + \nu_n)$ accompanied by the transition of the molecule, on which scattering occurs, to a state with energy lower by $h\nu_0$. Since molecular energy is quantized, losses of photon energy are also quantized [18].

Recent developments of Raman spectroscopy have made this technique one of the most sensitive analytical tools. Raman measurement gives the vibrational spectrum of the analyte that can be treated as its “fingerprint” and allows for its easy identification. Raman signal can be collected with a small probe head linked to the (portable) Raman apparatus by the optical fiber. Therefore, Raman analysis can be comfortably carried out at different locations of even very large objects [19].

7. Flow Injection Analysis

FIA is a mature technique with well-defined and explored principles of operation. In brief, a defined sample zone is injected directly into a continuously moving stream of a carrier or reagent. Chemical or physical manipulation of the sample takes place in an on-line mode as it flows inside the manifold towards the detector [20].

The modern Flow Injection Analysis system usually consists of a high quality multichannel peristaltic pump, an injection valve, a coiled reactor, a detector such as a photometric flow cell, and an autosampler. Additional components may include a flow through heater to increase the speed of chemical reactions, columns for sample reduction, debubblers, and filters for particulate removal [21].

FIA offers the following advantages: simplicity and low cost instrumentation, availability of instrumentation in almost all laboratories, high sampling rate, reduced analyses cost when a lot of samples have to be analyzed, increased precision compared to batch methodologies and automation in sample preparation and detection.

In recent years, FIA has been supple-mented by SIA (Sequential injection Analysis) and LOV (Lab-on-Valve), which methods have furnished additional features to the original FIA-concept. Sequential Injection Analysis (SIA) is the second generation approach to FIA compatible assays. SIA usually consists of a single-channel high precision bi-directional pump, a holding coil, a multiposition valve, and a flow through detector. The system is initially filled with a carrier stream into which a zone of sample and a zone of reagent(s) are sequentially aspirated into a holding coil, forming a linear stack. These zones become overlapped due the parabolic profile induced by differences between flow velocities of adjacent streamlines. Flow reversals and flow acceleration further promote mixing. The multiposition valve is then switched to the detector position, and the flow direction is reversed, propelling the sample/reagent zones through the flowcell.

The advantage of SIA over the more traditional flow injection analysis (FIA) is that SIA typically consumes less than one-tenth the reagent and produces far less waste – an important feature when dealing with expensive chemicals, hazardous reagents, or online/remote site applications. One disadvantage of SIA is that it tends to run slower than FIA [21].

Spectrophotometric detection in its various manifestations is probably the most widely used method of detection in flow-based analysis. The development of cheap, robust detectors based on LEDs and photodiodes, and the availability and increasing utilisation of fibre optics and compact, modular, reasonably priced array detectors further reinforces the role that spectrometry has as the workhorse detection method in FIA and other emergent flow-based techniques [22].

8. Conclusions

A quick glance at today’s instrumentation market indicates the popularity of the array detector as the detector of choice. Because of their unique combination of outstanding sensitivity, high speed, low noise, compactness, instantaneous capture of full spectra, low cost and robustness, these detectors have revolutionized spectroscopic detection.

The fluorescence spectroscopy has also an important place in the field of today spectroscopy. The characteristic feature of this method is very high sensitivity and often also an outstanding selectivity, which makes the fluorescence spectroscopy the method of choice.

Automation is a key demand in modern
analytical chemistry. Process and quality control require fast and reliable results in all areas of human activity. On this field, FIA offers unique features and advantages.

References


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