ACOUSTO-OPTIC TUNABLE FILTER: A NEW GENERATION MONOCHROMATOR AND MORE

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ABSTRACT

The acousto-optic tunable filter is a compact, all solid state electronic monochromator. It is based on the acousto-optic interaction in an anisotropic crystal. Compared to conventional grating monochromators, the AOTF has no moving parts, wider spectral tuning range (from UV though visible and near-IR to IR), higher throughput, higher resolution (few angstroms), faster scanning speed (μs) and imaging capability. These features make it possible to use the filter to develop novel instruments which are not possible otherwise. The instrumentation
development and unique advantages of such AOTF based instruments including a multidimensional fluorimeter, detectors for HPLC and flow injection analysis, and a multispectral imaging instrument are described.

INTRODUCTION

An acousto-optic tunable filter (AOTF) is an all-solid state, electronic dispersive device which is based on the diffraction of light in an anisotropic crystal\textsuperscript{13}. Light is diffracted by an acoustic wave because an acoustic wave propagating in a transparent material will produce a periodic modulation of the index of refraction (via the elasto-optical effect). This, in turn, will create a moving grating which diffracts portions of an incident light beam. The diffraction process can, therefore, be considered as a transfer of energy and momentum. Conservation of the energy and momentum must, therefore, be maintained. The equation for conservation of momentum can be written as\textsuperscript{1}:

$$k_d = k_i \pm k_s$$

(1)

where $k_s$, $k_d$, and $k_i$ are the wave vectors of the incident and diffracted light, and of the phonon.

Because in this case the acousto-optic interaction occurs in an anisotropic medium, and the polarization of the diffracted beam is orthogonal to that of the incident beam, the momenta of incident and diffracted photons can be written as:

$$|k_i| = \frac{2\pi n_i}{\lambda}$$

(3)

$$|k_d| = \frac{2\pi n_d}{\lambda}$$

(4)
They are, therefore, not equal since one is an ordinary ray and the other is an extraordinary ray (i.e., \( n_i \neq n_g \)).

Depending on the propagating direction of the light and sound waves in the crystal, AOTF can be divided into two types: collinear and non-collinear AOTF. In the collinear AOTF, the incident and the diffracted light beams, and the acoustic beam are all collinear. If the incident light is an extraordinary and the diffracted light is an ordinary ray, the momentum matching condition becomes:

\[
\mathbf{k}_d = \mathbf{k}_i - \mathbf{k}_\lambda
\]

\[
f_s = \frac{v_s(n_e - n_0)}{\lambda}
\]

where \([k_i] = (2\pi f_i)/v_s\) which \(f_i\) and \(v_s\) are the frequency and velocity of the acoustic wave. Equation 6 can be generalized for all types of AOTFs including the collinear and the noncollinear AOTFs:

\[
\lambda = \frac{v_s(n_e - n_0)(\sin^4 \theta_i - \sin^2 2\theta_i)^{\frac{1}{2}}}{f_s}
\]

where \(\theta_i\) is the incident angle. When \(\theta_i = 90^\circ\) eq 7 reduced to eq 6, i.e., the case of collinear.

It is, thus, evidently clear that in an anisotropic crystal where the phase matching requirement is satisfied, diffraction occurs only under optimal conditions. These conditions are defined by the frequency of the acoustic waves and the wavelength of a particular diffracted light. For a given acoustic frequency (i.e., \(f_s\)), only light whose wavelength \(\lambda\) satisfies either eq 6 or eq 7 is diffracted from the crystal. The filter can, therefore, be spectrally tuned by changing the frequency of the acoustic waves (i.e., \(f_s\)).
Generally, the AOTF is fabricated from an anisotropic TeO$_2$ crystal onto it an array of LiNbO$_3$ piezoelectric transducers are bonded. A radio frequency (RF) signal is applied to the transducers which, in turn, generates an acoustic wave propagating through the TeO$_2$ crystal. These propagating acoustic waves produce a periodic moving grating which will diffract portions of an incident light beam. A light beam propagating as an e-ray is converted into an o-ray and in addition, is spatially separated from the original e-ray by interaction with, and diffraction from, an acoustic wave propagating in the same medium. As illustrated in equation 7, for a fixed acoustic frequency $f$, and sufficiently long interaction length, only a very narrow band of optical frequencies can approximately satisfy the phase matching condition and be diffracted. Shown in Figure 1 are two types of AOTF: collinear AOTF and noncollinear AOTF. In the collinear AOTF, the acoustic wave and the optic beam collinearly propagate in the crystal. The diffracted beam is spatially the same, but polarization is perpendicular to that of the to the transmitted beam (Figure 1a). In the noncollinear type, the acoustic wave traverses across the optical beam. The diffracted beam is spatially separated from the transmitted beam. Because the AOTF crystal is anisotropy, depending on the polarization of the incident beam (i.e., linear or un-polarized) one or two beams can be diffracted from the filter (Figure 1b and 1c). The wavelength of the diffracted light can therefore be tuned over large spectral regions by simply changing the frequency of the applied RF signal. The scanning speed of the filter is, therefore, defined by the speed of the acoustic wave in the crystal, which is on the order of microseconds. As a consequence, compared to conventional gratings, the AOTFs offer such advantages as being all-solid state (contains no moving parts), having rapid scanning ability (μs), wide spectral tuning range and high throughput, allowing high speed random or sequential wavelength access, and giving high resolution (a few Å). The AOTF has offered unique means to develop novel instruments which are not possible otherwise. Some of unique AOTF based instruments will be described in the following sections.
Fig. 1: Types of acousto-optic tunable filter: (1) collinear, noncollinear with linear polarized incident light, and (c) noncollinear with unpolarized light.
APPLICATIONS

AOTF as a Fast, Electronic Monochromator, Electronic Shutter and Light Intensity Stabilizer

As described in the previous section, the wavelength of the light diffracted from an AOTF can be tuned over a large optical region by simply changing the frequency of the applied rf\textsuperscript{3}. The intensity of the diffracted light is known to be dependent on frequency and power of the applied RF signal. These features made it possible to use the AOTF not only for rapid spectral tuning of a light source but also for amplitude modulation and stabilization\textsuperscript{4}. These were accomplished by rapidly scanned the frequency of the RF signal applied into the AOTF (for rapid spectral tuning)\textsuperscript{4}. Judicious selection of the frequencies and power of the applied RF enabled the AOTF not only to rapidly scan the diffracted beam from one wavelength to the other, but also to provide the amplitude modulation for the beam\textsuperscript{4}. Furthermore, the diffracted beam can be turned off when no RF signal (or when an RF signal which does not correspond to any of the wavelengths of the incident light) is applied to the filter. The filter can, therefore, be used as a fast electronic shutter and an AM modulator\textsuperscript{4}. By splitting part of the diffracted beam into a reference photodiode to build a feedback loop, the AOTF can be used to amplitude stabilize the intensity of the diffracted beam. Specifically, the intensity of the diffracted beam can be maintained at a constant level by controlling either the frequency or the power of the applied RF signal through the feedback mechanism\textsuperscript{4}.

It is important to realize that the light diffracted from the AOTF needs not be monochromatic\textsuperscript{1}. Multiwavelength light can be diffracted from the rf when several rf signals are applied into the AOTF. The number of colors in the diffracted beam corresponds to the number of the rf signals which are applied into the filter. Because the intensity of each color in the diffracted beam is dependent on the frequency and the power of the corresponding rf signal, the AOTF can, in principle, be used to stabilize the intensity of each color of the multiwavelength laser beam. In fact, a new method has been developed in which the AOTF was used to stabilize
the amplitude of a multiwavelength laser beam. In this method, the AOTF was used to diffract light which has more than one wavelength. The number of the wavelengths in the diffracted light is controlled by the number of the rf signals which are applied into the filter. Because the intensity of each wavelength in the diffracted beam is dependent on the power of the corresponding applied rf signal, the total amplitude of the multiwavelength diffracted beam can be stabilized, i.e., adjusted at a constant amplitude and maintained at that level, by individually controlling the intensity of each corresponding wavelength by use of a rf driver with a feedback loop for each wavelength. In addition, the method also provides a unique means to amplitude-modulate one (or more) wavelength(s) of a multiwavelength beam at a specific frequency while keeping the other wavelengths at a constant amplitude level. It is noteworthy to add that this type of advanced, sophisticated and selective manipulation of each wavelength of a multiwavelength beam can only be achieved with the present AOTF method, because other stabilization methods, including the electro-optic modulators, can only be used to control the intensity of a monochromatic beam. The method is not restricted to lasers but rather can be used for other types of light sources including incandescent and arc lamps.

AOTF as a Polychromator: Multidimensional Fluorimeter

Fluorescence is one of the most sensitive techniques for trace chemical analysis. Since realtime samples are generally mixtures of many different compounds, it is often necessary to measure fluorescence spectra at different excitation wavelengths (because absorption spectra of compounds in the mixture are different). A fluorimeter based on multichannel detection (e.g., videofluorimeter) has been developed to alleviate this time consuming process. While the instrument has proven to be a very powerful method for the determination of multicomponent trace chemical species, its applications are still limited because of such factors as high cost, low sensitivity, slow in the data acquisition (the fastest is on the order of milliseconds) and complicated data analysis. These limitations
can be eliminated if the AOTF is used to develop a new generation multidimension spectrofluorimeter.

As explained above, an incident white light is diffracted by the AOTF into a specific wavelength when a specific RF is applied to it. The diffracted light needs not be a monochromatic light. Multiwavelength light can be diffracted from the AOTF when more than one RF signal is simultaneously applied into the filter. As a consequence, the AOTF can be used as a polychromator. Compared to conventional polychromators, advantages of this electronic AOTF polychromator include its ability to individually amplitude-modulate each wavelength of the diffracted multiwavelength light at different frequency. This is accomplished by individually and sinusoidally modulating each applied RF signal at a different frequency. This feature, together with the fast scanning ability, make the AOTF uniquely suited for the development of a novel, all solid-state, nonmoving parts multidimensional spectrofluorometer.

Two AOTF's were used in the AOTF based multidimensional fluorimeter: one for excitation and the other for emission. The first AOTF was used to specifically diffract white incident light into a specific wavelength(s) for excitation. Depending on the needs, the second AOTF (i.e., the emission AOTF) can be used as either a very fast dispersive device or a polychromator. In the first configuration (i.e., the rapid scanning fluorimeter), the sample was excited by a single excitation wavelength; the emitted light was analyzed by the emission AOTF which was scanned very fast. A speed of 4.8 Å/μs was found to be the fastest at which the AOTF can be scanned with a reasonable S/N and resolution. With this speed, a spectrum of 150 nm can be measured in 312 μs. Faster scanning is possible. However, because of the limitation due to the speed of the acoustic wave, such scanning may undesirably lead to the degradation in the S/N and spectral resolution.

In the second configuration (i.e., multidimensional fluorimeter), both AOTFs were used as polychromators. Several different rf signals were simultaneously applied into the first AOTF to provide multiple excitation wavelengths. The
emission was simultaneously analyzed at several wavelengths by the emission AOTF. It was possible to use the fluorimeter for the simultaneous determination of multicomponent samples. In principle, the maximum number of components which the fluorimeter can analyze is \(a \times b\) where \(a\) and \(b\) are the number of excitation and emission wavelengths, respectively\(^7\). In fact, by use of a fluorimeter which has \(a = b = 2\), we successfully analyzed samples containing four different components (rhodamine B, fluorescein, eosin and 4-(dicyanomethylene)-2-methyl-6-[p-(dimethylamino)styryl]-4-H-pyran (DMP)) with detection limit of \(10^{-10}\) M \(^8\).

**Near Infrared Spectrometer with High Light Throughput: Spectrometer based on the AOTF and an Erbium Doped Fiber Amplifier**

NIR has been used extensively in recent year for chemical analysis. The popularity stems from the advantages of the technique, namely its wide applicability, noninvasive and on-line characteristics. The near infrared region covers the overtone and combination transitions of the C-H, O-H and N-H groups, and since all organic compounds possess at least one or more of these groups, the technique is applicable to all compounds\(^9\). There is no need for pretreatment of the sample, and since NIR radiation can penetrate a variety of samples, the technique is noninvasive and has proven to be potentially useful for noninvasive, on-line measurements. However, analytical applications of the NIR have not been as widely as expected from its potentials. This may be due to a variety of reasons but the most likely ones are probably due to the limitations on the speed, stability and light throughput of the currently available instruments. To be effectively used as a detector for on-line measurements, the NIR instrument needs to have high and stable light throughput, to suffer no drift in the baseline, and can be rapidly scanned. These impose severe limitations on conventional NIR spectrophotometers because such instruments generally have relatively low and unstable light throughput, suffer some degree of baseline drift, and can only be scanned very slowly. AOTF, with its ability to rapidly scan as well as to control and maintain the
intensity of light at a constant level, offers a means to alleviate some of these limitations.

It has been shown recently that stimulated emission can be achieved in a fiber when the fiber is doped with rare earth ions such as Er³⁺, and optically pumped by a diode laser¹⁰. Now, for the first time, a lasing medium can be confined in a material as flexible and as small (less than 10 μm) as a single mode fiber. Because of such features, the length of the erbium doped fiber can be adjusted to as long as a few miles to enable the fiber to have optical output in the range of kilowatts. Furthermore, the high power diode pump laser can be fusion-spliced directly into the erbium doped fiber. It is thus, evidently clear that this all-fiber, compact erbium doped fiber amplifier (EDFA) can provide NIR light with highest intensity and widest spectral bandwidth compared to other (cw) near-IR light sources currently available. By use of this novel NIR light source, it was reported recently that a novel, compact, all solid state, fast scanning near infrared spectrophotometer which has no moving parts, high and very stable light throughput can be developed by synergistical use of this EDFA as a light source and AOTF as a dispersive element¹¹.

As expected, the sensitivity of this EDFA-AOTF based spectrophotometer is comparable with those of the halogen tungsten lamp-AOTF based instruments, i.e., this spectrophotometer can detect water in ethanol at a limit of detection of 10 ppm. More importantly is its high light throughput. The intensity of this EDFA light source was found to be about 20 times higher than that of 250 W halogen tungsten lamp. As a consequence, it can be used for measurements which are not possible with lamp based instruments. Two measurements were performed to demonstrate this advantage. In the first measurement, the intensity of the light transmitted through 6 sheets of photocopy paper (Cascade X-9000 white paper) was measured. Because of the high absorption (of the papers) and low intensity (of the halogen tungsten lamp) no light was transmitted when the halogen tungsten lamp based spectrophotometer was used. Because of its high intensity, a substantial amount light was transmitted through the papers¹¹. In the second measurement, it
was not possible to use a lamp based spectrometer to measure absorption spectrum of 1.0 M solution of Pr$^{3+}$ in D$_2$O (in a 2-mm cell) placed after 4 sheets of photocopy paper (dashed line). Because of its high intensity, substantial amount of EDFA light was transmitted through the papers and Pr$^{3+}$ solution, and as a consequence, absorption spectrum of the latter can be recorded. This high throughput advantage is of particular importance in NIR measurements because NIR techniques are often used for measurements in which the signal of interest is very small, riding on top of a very large background signal. As such, it is very difficult, inaccurate and sometimes not possible to perform such measurements with low-light-throughput spectrophotometers.

Rapid advances in fiber optic technology have made it possible for scientists to integrate optical and acousto-optical components (integrated acousto-optics). Activities in this field, which is based on the Bragg interactions between waveguide and surface acoustic waves, have increased significantly in recent years. As a consequence of the theoretical and experimental work, integrated AOTFs (IAOTFs) have been developed. This device is based on the photoelastic effect where surface acoustic waves (SAWs) diffract light from one polarization state to another. Similar to bulk acousto-optic interaction, the polarization conversion is extremely wavelength specific. The required acoustic power is, however, substantially less than bulk devices because the SAWs can be confined in an acoustic waveguide. The scanning speed of the filter is relatively shorter (less than 10 μs) than those of the bulk AOTFs (because of the shorter distance the acoustic wave has to travel in the IAOTF). However, this disadvantage was overcome by judiciously using the filter for measurements in which its tuning range is coincident with the light source and also with absorption bands of analytes. In fact, an all fiber, compact, high throughput near infrared spectrophotometer has been successfully constructed by synergistic use of this integrated AOTF and the EDFA. This all fiber spectrometer has proven to be sensitive, to have high intensity and high throughput in the NIR region from 1500 to 1600 nm. This
spectral region is particularly useful for the determination of samples which have O-H and/or N-H groups. The spectrometer is particularly suited for the on-line and in real-time detection of trace gases in a hostile environment including the leak detection of monomethylhydrazine (at a limit of detection of 191 ppm) which is often used as the hypergolic propellants for the Space Shuttle thruster systems\textsuperscript{13}.

**AOTF based Detectors for HPLC and Flow Injection Analysis**

**AOTF based Detector for HPLC**

High performance liquid chromatography (HPLC) has increasingly become the technique of choice for chemical separations. As the technique becomes more prevalent the demand for detectors, that can provide quantitative as well as qualitative information on the analyte, increases.

UV-visible absorption detectors are currently the most widely used detectors. However, this type of detector can only be used as a quantitative technique because the qualitative information obtained from this detector is rather limited, namely, it relies on the use of the retention time for sample identification. The development of diode array detectors (DADs) in the early 1980's made it possible to obtain qualitative and quantitative information on a sample. Specifically, with a DAD detector, the spectrum obtained for each peak in the chromatogram can be stored, and the subsequent comparison with standard spectra will facilitate the identification of peaks\textsuperscript{14}. Unfortunately, in spite of their advantages, DADs still suffer from limitations including their relatively high cost and their low sensitivity (compared to variable and fixed wavelength detectors)\textsuperscript{14}. It is therefore, of particular importance that a novel detector which has higher sensitivity, low cost and possesses all of the DADs' advantages be developed. The AOTF with its unique features is particularly suited for the development of such a detector. Specifically, with its microsecond scanning speed, the AOTF based detector can rapidly record absorption spectrum of a compound as it elutes from the column. The random access to wavelength(s) makes it possible to change and/or to program
the detector to any wavelength(s) to obtain optimal detection. However, different from the DADs, the AOTF-based detector is a single channel detection technique, i.e., it is based on a photomultiplier tube. Its sensitivity is, therefore, higher and its cost is lower than the multichannel detectors (i.e., DADs).

A AOTF based detector for HPLC has, in fact, been developed. The detector, based on the use of a 150-W xenon arc lamp, was used as the light source and a collinear quartz AOTF, which has spectral tuning range from 250 to 700 nm, as the dispersive element. AM modulation of the applied RF signal facilitates phase lock detection\(^\text{15}\).

The detector makes it possible to plot the chromatogram in a three-dimensional plot, namely, the absorbance of a mixture of compounds was plotted as a function of time and wavelength. The chromatogram as a function of time was obtained by setting the AOTF at a single wavelength. Absorption spectrum of each compound was measured as it eluted out of the column by rapidly scanning the AOTF\(^\text{15}\). Shown in Figure 2 is the chromatogram of the sample which contains a mixture of pentachloro-, trichloro- and 4-chlorophenol plotted as a function of time and wavelength. In this case, each absorption spectrum is the average of 20 spectra taken on the same compound (of the same mixture) as it went though the chromatographic cell. Each single absorption spectrum was obtained by scanning the AOTF for 100 nm (e.g., from 250 nm to 350 nm) and recording 100 points (i.e., 1 point for each nanometer). In the reported chromatogram, it took 2 ms to record each point. Therefore, the time required to record a single spectrum is 200 ms, and it took 4 s to obtained the spectrum which is the average of 20 spectra for each compound. However, the recording time can be readily reduced to 900 ms for a spectrum which is an average of 5 spectra\(^\text{15}\).

In addition to the fast scanning ability, the detector has high sensitivity. The limits of detection (LODs) for trichloro-, pentachloro- and 4-chlorophenol were found to be 1.0 X 10\(^{-5}\), 1.1 X 10\(^{-5}\) and 1.7X 10\(^{-3}\) M, respectively. These LOD values correspond to the mass detectivity of 59, 88 and 65 ng, respectively, and to
Fig. 2: Three dimensional graph plotting the chromatogram of mixture of pentachloro-, trichloro- and 4-chlorophenol as a function of time and wavelength.

the absorbance unit of $4.0 \times 10^{-4}$ AU. These detections limit are comparable with UV-visible variable (single wavelength) detectors.

More importantly, the LOD value of $4.0 \times 10^{-4}$ AU obtained with this AOTF based detector is much smaller than those obtained using commercially available diode array detectors. This high sensitivity can be due to the fact that the AOTF based detector is a single channel detection technique which is more sensitive than the multichannel detection employed in the diode array detectors. Furthermore, the light source used in the AOTF based detector is AM modulated. This facilitates the phase lock detection which, in turn, enhances the S/N. Other features which makes this AOTF-based detector more desirable than diode array detectors is its high spectral resolution. Specifically, the resolution of the AOTF-based detector is reported to be $0.82 \, \text{Å}$ at 253 nm. This spectral resolution is much smaller than those of the DAD which are generally on the order of several nanometers.
AOTF based Detectors for Flow Injection Analysis

Flow injection analysis (FIA) is among the most widely used methods for automated analysis. Its applications to several fields of chemistry have been demonstrated in recent years. Several operational modes of FIA have been realized by appropriately modifying traditional wet chemical methods (dilution, extraction, titration, fast kinetic reactions) into automated flow devices\textsuperscript{16-19}. Different types of detectors, including electrochemical, (UV and visible) spectrophotometric, and luminescent, have been applied to the FIA\textsuperscript{16-19}. However, there has not been a FIA detector which is truly universal.

Near-infrared (NIR) spectrometric techniques are known to have wide applications (all compounds that have C-H, O-H and/or N-H groups have absorption in this spectral region), non invasive and non-destructive capability. These advantages enable the NIR to serve as a universal detector for FIA. AOTF based NIR detector for FIA has, in fact, been developed. This detector was based on the use of a 100-W, 12-V halogen tungsten lamp as the light source, a non-collinear TeO\textsubscript{2} AOTF as the dispersive element, and InGaAs photodiode as the detector\textsuperscript{20}. This AOTF based detector covers the NIR region from 1000 to 1600 nm. Because the combination and overtone absorption bands of O-H and C-H groups are in this region, trace amounts of water in chloroform as well as trace amounts of water and benzene in ethanol were successfully detected using this FIA-AOTF detector\textsuperscript{20}. For example, Figure 3 shows the absorption measured as a function of time and wavelength after the injection of ethanol samples containing 0.6 and 1.5 % of water and benzene, respectively. As can be seen from the figure, when the sample is passing through the detector between 8 to 26 seconds there is an increase in the absorption in the 1650-1700 nm and 1390-1500 nm regions (due to absorption of benzene and water, respectively) and a decrease in the 1500-1650 nm region (due to benzene). Good correlation was obtained between the concentration of water and benzene injected and the concentration of both components. The statistical parameters obtained were $r = 0.997$ and $\text{RMSD} = 0.015 \%$ and $r = 0.997$ and $\text{RMSD} = 0.033 \%$ for water and benzene, respectively\textsuperscript{20}. 
Fig. 3: Absorption (flow cell using ethanol as blank) as a function of time and wavelength measured after the injection of ethanol solution containing 0.6% and 1.5% (v/v) of water and benzene, respectively.

In summary, it has been demonstrated that due to its high scanning speed and wavelength accuracy the AOTF based detector for FIA can measure whole NIR spectra of flowing samples within the time frame required for flow analysis. This allowed the utilization of multivariate statistical methods of analysis, which in turn, increase the sensitivity, accuracy and applicability of the technique. It was possible to perform not only a simple analysis, such as the determination of dryness of organic solvent (i.e., the concentration of water in chloroform) but also a more complex analysis including the simultaneous determination of two component systems (i.e., the concentration of water and benzene in ethanol). For simple one
component systems, the LOD of this AOTF-NIR-FIA technique is comparable to that of the FIA spectrophotometry as well as to that of the single wavelength NIR-FIA technique. In this case the advantages of the AOTF-NIR-FIA instrumentation are its sensitivity, automation and wide applicability. For relatively more complex systems (e.g., two component systems) the advantages become more prevalent. In fact, there is not a method currently available that can be easily coupled with FIA instrument for the sensitive and simultaneous determination of the concentrations of two or more components without any sample pretreatment.

**AOTF based Multispectral Imaging**

Multispectral imaging spectrometer is an instrument which can simultaneously record spectral and spatial information of a sample, i.e., the recorded images contain signals that are generated by molecules or units in a sample, plotted as a function of spectral and spatial distribution. Chemical distribution in a sample or chemical compositions of several samples can be elucidated from such images. The type information is of particular importance since it is known that chemical as well as physical properties of materials are dependent on the chemical distribution within the samples. As a consequence, considerable efforts have been made in the last few years to develop multispectral imaging instruments. In these instruments, a camera is used to record the spatial distribution of the sample, and the spectral information is gained by scanning a dispersive device to record spectra for each image. AOTF with its unique advantages, particularly, its wide spectral tuning range (from visible to NIR), fast scanning ability, compact and non moving part, is particularly suited as a dispersive scanning device for the multispectral imaging instrument. In fact, an AOTF based multispectral imaging spectrometer has been developed. The schematic diagram of the instrument is shown in Figure 4. As illustrated, in this instrument, a 250-W halogen tungsten lamp was used as a light source. A non-collinear TeO$_2$ AOTF with a spectral tuning range of 650-1700 nm was used as a dispersive scanning device. The wide spectral tuning range of the AOTF together with its unique
Fig. 4: Schematic diagram of the AOTF based multispectral imaging spectrometer: AOTF, acousto-optic tunable filter; RF, rf signal generator; CCD, charge coupled device camera for the visible.

feature were utilized in this instrument to facilitate simultaneous recording of the visible and NIR region. Specifically, because the AOTF crystal is anisotropic, an incoming unpolarized light will be diffracted by the AOTF into two beams (ordinary and extraordinary beam) with orthogonal polarization. It is, therefore, possible for the multispectral imaging instrument based on the AOTF to simultaneously record images of a sample in the visible as well as in the NIR regions. This was accomplished by using an unpolarized light to incident onto the AOTF to produce two diffracted beams; one of the diffracted beam was used for the recording of images in the visible region (with a silicon CCD camera) and the other beam for the NIR images recorded with an InGaAs camera. Two RF
generators (one for the visible and the other for the NIR) were used to simultaneously drive the AOTF\textsuperscript{22}.

The multispectral imaging instrument was successfully used for the non-destructive measurement of absorption spectra of documents including currency. For example, it was shown that the ink used in the letter “L” on the US $1 bill is different from that in the letter “G” of the $5 bill, namely, the former has absorption in the visible and NIR region whereas the latter has only absorption in the visible region\textsuperscript{22}. It is, therefore, clear that the imaging instrument can be used not only for the authentication of documents (currency, stock certificates) but also as quality control and assurance method.

The high sensitivity and fast scanning ability of the multispectral imaging spectrometer make it suitable for kinetic determination of fast reactions. It was successfully used to determine kinetics for curing of epoxy (poly(bisphenol-A-co-epichlorohydrin) glycidyl end capped) by amine (diethylenetriamine). As expected, the kinetic data obtained using the imaging instrument agrees well with those obtained by FT-IR. The imaging spectrometer thus, possesses all advantages of conventional NIR spectrometers. It has, however, additional features which conventional IR spectrometers cannot offer, namely, its ability to provide kinetic information at different positions within a sample. The high spatial resolution and sensitivity of the NIR InGaAs camera make it possible to determine the kinetic from data collected by a single pixel in the camera. Kinetic of curing of epoxy by amine, determined by this multispectral imaging instrument shows that the reaction rates within the sample are very inhomogeneous, and because of this inhomogeneity the differences in the degrees of cure reached at different positions within the sample can be as high as 37\%\textsuperscript{23}.

The multispectral imaging instrument was also used for the first time, to monitor solid phase peptide synthesis\textsuperscript{24}. As in the previous study to determine the kinetics of curing of epoxy by amine, this imaging instrument possesses all the advantages of conventional NIR spectrometers, namely, it can be used for the non-invasive monitoring of the reactions and identification of the products during the
solid phase peptide syntheses of glycine, alanine and valine mediated by aminomethylstyrene resin beads. The reaction was determined by monitoring either the decrease of the band at 1529 nm which is due to the amine group on the beads or the increase of the amide band at 1483 nm. The amine band at 1529 nm was also used to determine the presence of the Fmoc protecting groups, and the efficiency of its removal. More importantly, this imaging spectrometer has additional features which conventional NIR spectrometers cannot offer, namely, its ability to measure spectra at different positions within a sample. This feature was utilized for the first demonstration in which reactions of three different solid phase peptide syntheses (in a three-compartment cell) were simultaneously monitored. As expected, the kinetics obtained for three reactions are similar to those obtained when the each of the reactions was individually determined. As pointed out in the paper, the number of compartments of the cell used for this study is not limited to three. Multicompartment cells including those used in the combinatorial chemistry (e.g., cell with 96 X 96 compartment) can be used. Furthermore, in this study, up to 16 X 16 pixels were used to calculate a spectrum for each sample. However, as demonstrated in the epoxy study, relatively good spectrum can be obtained by using data recorded by a single pixel. Since the NIR camera used in this study is equipped with 240 X 320 pixels, it is evident that this multispectral imaging technique can be effectively used as the detection method for the solid phase peptide synthesis in the combinatorial chemistry. That is this imaging spectrometer should be able to simultaneously monitor solid phase peptide syntheses in a multicompartment cell equipped with 96 X 96 compartments or more.

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REFERENCES

21. M. D. Morris “Microscopic and Spectroscopic Imaging of the Chemical


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