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Principles and Analytical Applications of Acousto-Optic Tunable Filters

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Abstract : Acousto-optic tunable filter is a compact, all solid state electronic dispersive device. 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 through visible and near-IR to IR), higher throughput, higher resolution, faster scanning (μs) and random wavelength access. These features make it possible to use the filter to develop novel instruments which are not possible otherwise. The instrument development and unique advantages of such AOTF based instruments including the multidimensional fluorimeter, the multiwavelength thermal lens spectrometer, and the detectors for HPLC and flow injection analysis are described.

Keywords : Acousto-optic tunable filter; fluorescence; thermal lens; high-performance liquid chromatography; flow injection analysis.

1. Introduction

Acousto-optic tunable filter (AOTF) is an electronic monochromator. It is based on the acousto-optic interaction in an anisotropic medium [1]. Generally, the filter 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. Under certain condition, a light beam propagating as an e-ray can, under some conditions, be converted into an o-ray and in addition, be spatially separated from the original e-ray by interaction with, and diffraction from, an acoustic wave propagating in the same medium [1]. The phase matching condition (i.e., conservation of momentum) must be satisfied in order for this conversion to be cumulative [1]. As a consequence of this conservation of

momentum, for a fixed acoustic frequency and sufficiently long interaction length, only a very narrow band of optical frequencies can approximately satisfy the phase matching condition and be diffracted. 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 AOTF is thus similar to the diffraction grating. One of the obvious advantages of the AOTF is that the grating constant, which in this case is the frequency of the acoustic wave, can be electronically changed. Rapid scanning of the filter is, therefore, possible. In fact, since the scanning speed of the AOTF is controlled by the transit time of an acoustic wave across an optical beam which is on the order of few microseconds, the tuning speed of the filter can be as fast as a few microseconds [1].

Advantages of the AOTF over a filter wheel or a grating monochromator include: (1) compact, all solid state, rugged and contains no moving parts; (2) wide acceptance angle; (3) wide tuning range (from UV through visible to IR); (4) high spectral resolution (bandwidth of light transmitted by the filter is less than 1 Å in the ultraviolet region); (5) rapid scanning ability (order of few μs); (6) high speed random or sequential wavelength access; (7) high throughput (diffraction efficiency of more than 90% can be achieved); and (8) imaging capability. The AOTF has been called "**the new generation monochromator**" and has offered unique means to develop novel instruments which are not possible otherwise. The instrumentation development and unique advantages of such AOTF-based instruments including the multidimensional fluorimeter, the multiwavelength thermal lens spectrometer, and detectors for HPLC and for flow injection analysis will be reported in this paper.

2. AOTF-based Fluorimeters

Fluorescence technique has been demonstrated to be a sensitive method for trace characterization. Since realtime samples are generally presence in multicomponent form, their analyses usually require measurements of the fluorescence spectra at different excitation wavelengths. This time consuming process was alleviated with the use of the videofluorimeter [6-7]. While the instrument has proven to be a very powerful method for the determination of multicomponent trace chemical species, its applications are still restricted because it suffers from such limitations as high cost, low sensitivity, slow in the data acquisition (the fastest is on the order of milliseconds) and complicated data analysis [6-7]. 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. It is important it realize that the diffracted light needs not be a monochromatic light. Multiwavelength light can be diffracted from the AOTF when more than one RF signals are simultaneously applied into the filter [1]. 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 to be uniquely suited for the development of a novel, all solid-state, nonmoving parts multidimensional spectrofluorometer.

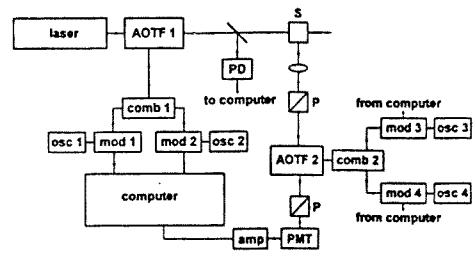

Fig 1. Schematic diagram of the AOTF based fluorometer: PD, photodiode; S, sample; P, polarizer; PMT, photomultiplier tube; amp, amplifier; osc, oscillator; mod, modulator; comb, combiner.

The schematic diagram of the AOTF based multidimensional fluorimeter is shown in Fig 1 [2,3]. Two AOTF's were used in this instrument: 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 speed 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, but because of the limitation due to the speed of the acoustic wave, may undesiredly lead to the degradation in the S/N and spectral resolution [2,3]. In the second configuration (i.e., multidimensional fluorimeter), both AOTFs were used as a polychromator. 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. With this configuration, the fluorimeter can be used for the analysis of multicomponent samples, and the maximum number of components it can analyze is, in principle, a X b where a and b are the number of excitation and emission wavelengths, respectively [3]. In fact, multicomponent samples e.g., mixtures of rhodamine B, fluorescein, eosin and 4-(dicyanomethylene)-2-methyl-6-[p-(dimethylamino)styryl]-4-H-pyran (DMP) can be simultaneously analyzed at a limit of detection of 10^{-10} M [2,3].

3. AOTF-based Thermal Lens Spectrophotometer

The fluorescence technique is very sensitive and can be used for the determination of trace chemical species at very low concentration. However, the technique is not applicable to all compounds because only few molecules are fluorescent. It is, therefore, important that novel technique which has the same sensitivity as the fluorescence technique but is applicable to non-fluorescent compounds be developed. Thermal lens technique is one of such possibilities.

The thermal lens technique is based on the measurement of the temperature rise that is produced in an illuminated sample by nonradiative relaxation of the energy absorbed from a laser [8-11]. Because the absorbed energy is directly measured in this case, the sensitivity of the technique is similar to that of the fluorescence technique, and is relatively higher than the conventional absorption measurements. In fact it has been calculated and experimentally verified that the sensitivity of the thermal lens technique is 237 times higher than that by conventional absorption techniques when a laser of only 50 mW power was used for excitation [8-11]. Absorptivities as low as 10^{-7} have been measured using this ultrasensitive technique [8-11]. Potentially, the technique should serve as an excellent method for trace chemical analysis because it has high sensitivity, in situ and non-destructive ability, and requires a minimum amount of sample. Unfortunately, its applications to the area of general trace chemical analysis are not so widespread in comparison to other spectrochemical methods. A variety of reasons might account for its limited use, but the most likely one is probably due to the low selectivity. The majority of reported thermal lens spectrometers employ only a single excitation wavelength [8-11], and as a consequence can only be used for the analysis of one component samples. A multiwavelength thermal lens spectrometer is needed to analyze, in realtime, multicomponent samples without any pretreatment. AOTF offers a unique means for the development of the first, all solid state, no-moving part fast scanning multiwavelength thermal lens instrument.

The schematic diagram of the first generation AOTF based multiwavelength thermal lens spectrometer is shown in Fig 2 [4]. An argon ion laser operated in the multiline mode was used as the excitation source. The AOTF was used to select the appropriate wavelength from the laser

beam, to provide the amplitude modulation of the diffracted beams, and to sequentially scan from one wavelength to other. The diffracted beam which was transmitted through the reference beamsplitter was focused onto the sample by an achromatic lens. The probe beam, provided by a He-Ne laser, was aligned to overlap with the pump beam at the sample cell by means of a dichroic filter (DF). The heat generated by the sample absorption of the pump beams changes the intensity of the probe beam. The intensity fluctuation of the probe beam was measured by a photodiode (PD2) placed behind a 632.8 nm interference filter (F) and a slit (S). A lens was used to focus the probe beam, and the distance between this lens and the sample was adjusted to give maximum thermal lens signals. The signal intensity, measured as the relative change in the probe beam center intensity, was recorded by a microcomputer through an AD interface board.

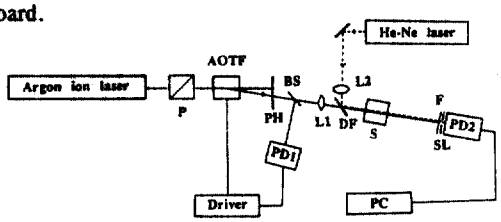

Fig 2. Schematic diagram of the AOTF-based multiwavelength thermal lens spectrometer: P, polarizer; PH, pinhole; BS, beamsplitter; DF, dichroic filter; F, interference filter; SL, slit; PD, photodiode.

Compared with other multiwavelength thermal lens instruments, this all solid state thermal lens spectrophotometer has advantages that include its ability to simultaneously analyze multicomponent samples in microsecond time scale, without the need for any prior sample preparation. In fact, with this apparatus and with the use of only 12 mW multiwavelength excitation beam, multicomponent samples including mixtures of lanthanide ions (Er^{3+}, Nd^{3+}, Pr^{3+} and Sm^{3+}) can be simultaneously determined with a LOD of 10^{-6} cm^{-1} .

4. AOTF based Detector for HPLC

High performance liquid chromatography (HPLC) has increasingly become the technique of choice for chemical separations. The popularity stems from the fact that with use of the appropriate stationary and mobile phases, all compounds can virtually be separated by this technique. As the technique becomes more prevalent the demand for detectors that can provide quantitative as well as qualitative information on the analyte increases.

Variable wavelength absorption detectors are the most widely used detectors for HPLC. However, HPLC with this type of detector can only be used as a quantitative technique because the qualitative information obtained from this type of detector is rather limited, namely, its relies on the use of the retention time as the only tool for identification. The development of diode array detectors (DADs) in the early 1980's made it possible to obtain information on peak purity and identity [13]. Specifically, when DAD is used as a detector for HPLC, 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 [12]. The optimum wavelength for single wavelength detection can easily be found [12]. Wavelength changes can be programmed to occur at different points in the chromatogram, either to provide maximum sensitivity for peaks, or to edit out unwanted peaks, or both [12]. 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). 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).

The schematic diagram of the AOTF based detector is shown in Fig 4. A 150-W xenon arc lamp was used as

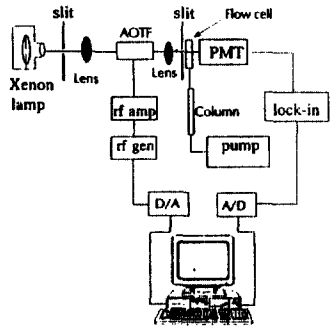

Fig 3. Schematic diagram of the AOTF based detector for HPLC: PMT, photomultiplier tube; lock-in, lock-in amplifier; rf, rf power amplifier; rf gen, rf signal generator.

the light source. Its output radiation which contains UV and visible light was focussed onto the AOTF by a combination of a reflector, collimator and lens. .Acoustic waves will be generated in the AOTF when the RF signal is applied into the filter by means of the Wavetek model 1062 signal generator. To reduce noise and to facilitate the phase sensitive detection the rf signal was sinusoidally modulated at 50 kHz by the microcomputer through the D/A. Prior to being connected to the AOTF, the AM modulated RF signal was amplified to 5 W power by an RF power amplifier. The intensity of the light diffracted from the AOTF was detected by a photomultiplier tube and demodulated (at 50 kHz) by a lock-in amplifier prior to being recorded by a microcomputer.

The chromatographic system consists of an isocratic pump and a sample injector valve equipped with a 40-μL loop. A 250 mm X 4.6 mm I.D. stainless-steel column packed with Nucleosil 5 silica was used. The chromatographic microflow cell used in this study, which has 8-mm path length and 8-μL volume, is similar to that used previously [10].

Shown in Fig 4 is the three dimensional graph plotting the chromatogram as a function of time and wavelength of a sample which was a mixture of three phenol derivatives, i.e., 4-chloro-, trichloro- and pentachlorophenol. The chromatogram as a function of time was obtained by setting the AOTF at a single wavelength of 292 nm. Absorption spectrum of each compound was measured as it eluted out of the column by rapidly scanning the AOTF. Each single spectrum was obtained by scanning the AOTF for 100 nm (from 250 nm to 350 nm) and recording 100 points (i.e., 1 point for each nanometer). The setting was selected so that it required 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, as evident from the figures, only 60 nm (i.e., from 260 nm to 320 nm) is required to record the whole spectrum for all three compounds. Therefore, with the optimal setting of 300 μs time constant, 12 dB rolloff, and 2 ms/pt (on the lock-in amplifier), it requires only 900 ms to obtain an average of 5 spectra which has relatively good S/N.

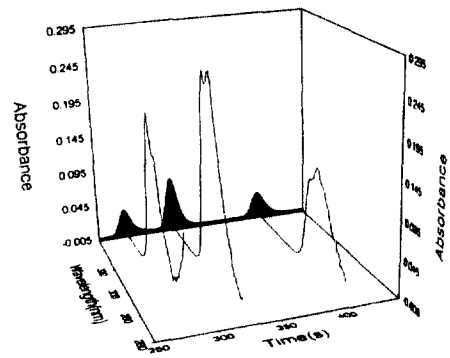

Fig 4. Three dimensional graph plotting the chromatogram of mixture of pentachloro-, trichloro- and 4-chlorophenol as a function of time and wavelength.

The calibration curve was constructed for each compound over a concentration range of 1.0 X 10^{-4} M to 2.0 X 10^{-3} M using the data obtained when the AOTF was

fixed at a single wavelength corresponding to the peak of the absorption spectrum of each compound, i.e., 285, 300 and 306 nm for 4-chloro-, trichloro- and pentachlorophenol, respectively. As expected, good linear relationship was obtained for all three compounds (the correlation coefficients for all three compounds were larger than 0.999). The limits of detection (LODs) defined as twice the peak-to-peak noise of the baseline divided by the slope of the calibration graph, are estimated to be 1.0×10^{-5}, 1.1×10^{-5} and 1.7×10^{-5} M for trichloro-, pentachloro- and 4-chlorophenol, respectively. These LOD values correspond to the mass detectivity of 59, 88 and 65 ng, respectively, and to the absorbance unit of 4.0×10^{-4}. These detections limit are comparable with those found on commercially available (grating or filter based) single wavelength absorption detectors. Particularly, its detectability of 4.0×10^{-4} absorption unit is similar to the value of 3.9×10^{-4} absorbance unit which we have previously determined for 4-chlorphenol using the Shimadzu model SPD-6AV UV-visible absorption detector [10]. The LOD value of 4.0×10^{-4} AU is much smaller than those obtained using commercially available diode array detectors [13]. This is as expected because the present 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 this AOTF based detector is modulated at 50 kHz (through modulating the applied RF signal) which facilitates the phase lock detection. The S/N is further enhanced by this phase sensitive detection. Other feature which makes this AOTF-based detector more desirable than diode array detectors is its high spectral resolution. Specifically, the resolution of this AOTF-based detector is less than one angstrom at 253 nm. This spectral resolution is much smaller than those of the DAD which are generally on the order of several nanometers [12].

5. 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 has been demonstrated in recent years. [13,14]. 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 [13,14]. Different types of detectors, including electrochemical, (UV and visible) spectrophotometric, and luminescent, have been applied to the FIA. [13,14]. However, there has not been a FIA detector which is truly universal.

Spectrochemical applications of the near infrared absorption technique (NIR) has increased significantly in recent years [15]. Several reasons are account for the popularity including the wide applicability (all compounds that have C-H, O-H and/or N-H groups have absorption in this spectral region), the possibility of in situ applications (no need for sample pretreatment) and the availability of powerful and effective multivariate statistical methods for data analysis [15]. These features enable the NIR to serve as a universal detector for FIA. However the detection of FIA by NIR has not been fully explored. In fact there is only one report describing the utilization of NIR for FIA detection [16]. Unfortunately, in this study the potentials of the NIR technique have not been fully exploited because it was based on the use of only a single wavelength. As a consequence, the multivariate calibration methods cannot be applied for data analysis [16].

Most of the NIR spectrophotometers are based on grating monochromators. Because of the low scanning speed of these devices it is not possible to measure whole spectral regions in the time frame necessary for FIA determinations. This drawback can be overcome by using acoustic optic tunable filter (AOTF).

In addition to the high resolution (less than 1 Å) [5] and no mechanical moving parts, the AOTF based spectrophotometer also has rapid scanning (μs) ability. These features make it ideally suited as a detector for FIA techniques.

The FIA system used in this experiment is similar to

those reported previously. Specifically, a peristaltic pump operating at a flow rate of 2 ml/min, pumped the solvent and the sample through the 100 μL sample injector to the 1.7 cm pathlength flow cell. The construction of the AOTF based NIR detector is essentially the same as that of the AOTF based UV-visible detector for HPLC which was described above. The only differences were those of the light source (a 100 W, 12 V halogen tungsten lamp), the AOTF for the NIR region, and a the detector (InGaAs photodiodes)

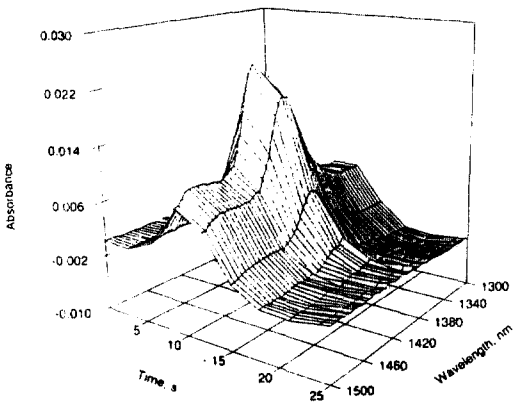

Fig 5. Three dimensional graph plotting the absorbance as a function of time and wavelength obtained when a chloroform solution containing 0.10 % of water was injected into pure chloroform.

This AOTF based detector covers a near IR region from 1000 to 1600 nm. Because the combination and overtone absorption bands of O-H and C-H groups are in this region, this FIA-AOTF detector can be used for such determinations as water in chloroform, and water and benzene in ethanol. Shown in Figure 5 is the FIA absorption peak profile (i.e., absorption spectrum as a function of time and wavelength), obtained when a solution of 0.10% (v:v) water was injected into chloroform. It is evident that as the concentration of water in the flow cell increases, there is an increase in the absorption in the 1300 - 1500 nm region. The can be attributed to the first overtone transition, and the combination of stretching and bending of the O-H group at 1450 and 1180 nm, respectively [17]. The absorption reaches its maximum 12 seconds after the injection and then starts to decrease. Using the spectra measured 12 seconds after the injection for different concentrations of water a calibration model based on the partial least square method (PLS) was developed for the determination of water in chloroform. Good correlation was obtained between the concentration of water injected and the concentration of water calculated by the model ($r = 0.99$). The RMSD for this determination was calculated to be 0.002 %. The LOD at 1400 nm was found to be 15 ppm of water.

Fig 6 shows the absorption measured against time and wavelength after the injection of a sample containing 0.16% of water and 0.04% of benzene. As can be seen from the figure, when the sample is passing through the detector (at about 12 seconds after injection) there is an increase in the absorption in the 1300-1450 nm region and a decrease in the absorption around 1200 nm. The increase observed in the 1300-1450 nm region is probably related to the presence of the stretching and bending combination transition of the C-H groups (of benzene) at around 1425 nm. This transition is at different wavelength than the same type of transition of the C-H groups of ethanol. For example, the λ_{max} values of the O-H first overtone band for H_2O and for ethanol were reported to be at 1425 and 1550 nm, respectively [17] (this is probably because of the fact that the 1550 nm band of ethanol is due not only to the O-H first overtone but also to the C-H combination band). The decrease observed at around 1200 nm can be explained by the decrease in the concentration of ethanol and consequently a decrease in its absorption in this region (with the increase in the concentration of added benzene). Both regions can be used to develop a PLS based calibration model for the determination of benzene and water in ethanol. Good correlations were found between injected and calculated concentrations of water and benzene. The statistical parameters obtained were $r = 0.99$, RMSD = 0.008% and $r = 0.97$, RMSD = 0.01% for water and benzene, respectively. The LODs for the simultaneous

determination of water and benzene in ethanol were found to be 16 and 16 ppm, respectively.

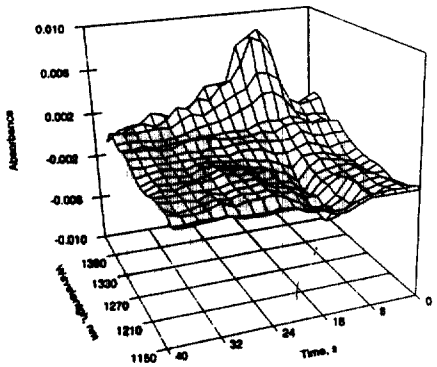

Fig 6. Three dimensional graph plotting absorbance as a function of time and wavelength obtained when an ethanol solution containing 0.12 % water and 0.04 % benzene was injected into pure ethanol.

As demonstrated because of the high velocity and accuracy of wavelength scanning obtained with the AOTF based monochromator, the whole NIR spectral region was obtained within the time frame required for flow injection analysis. This allowed the utilization of multivariate statistical methods of analysis which, in turn, increase the accuracy and applicability of the technique. In fact it was possible to perform not only a simple analysis, such as the determination of the 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). This type of automated and real-time determination of water and benzene in ethanol is important because ethanol is increasingly being used as a substitute and/or additive to gasoline (i.e., it is important to know the concentrations of water and benzene impurities in such systems).

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