Anal. Chem. **1997,** *69,* 1461−1464

Determination of Monomethylhydrazine with a High-Throughput, All-Fiber Near-Infrared Spectrometer Based on an Integrated Acoustooptic Tunable Filter and an Erbium-Doped Fiber Amplifier

Chieu D. Tran* and Guan-Hong Gao

Department of Chemistry, Marquette University, P.O. Box 1881, Milwaukee, Wisconsin 53201

A novel integrated acoustooptic tunable filter (IAOTF) has been developed. This tunable filter is based on the Bragg interactions between waveguide and surface acoustic waves. Compared to (bulk) AOTF, its advantages include all-fiber construction, smaller size, narrower spectral resolution (1.7 nm), higher diffraction efficiency (37%), and lower rf power requirement (150 mW). A relatively narrow spectral tuning range (about 80 nm) is the only drawback for this integrated tunable filter. 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 erbium-doped fiber amplifier (EDFA), which has been shown to provide high intensity and wide spectral bandwidth in the near-infrared 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 all-fiber nature, compactness, high throughput, and high sensitivity of this spectrophotometer make it particularly suitable for on-line and real-time detection of trace gases in hostile environments, including leak detection of monomethylhydrazine (at a limit of detection of 191 ppm), which is often used as the hypergolic propellant for the space shuttle thruster systems.

An erbium-doped fiber amplifier (EDFA) has been demonstrated to be an excellent source for the near-infrared region.[1] It is all-fiber, all-solid-state, compact, and reliable and requires little maintenance.[1] Its spectral bandwidth is wider and output intensity higher than those of other near-infrared (continuous-wave) sources which are currently available.[1] As a consequence, a near-infrared spectrophotometer based on EDFA can be used for measurements which are currently not possible with halogen−tungsten lamp-based spectrophotometers, including measurement of highly absorbing samples.[1] For example, we have recently demonstrated that the absorption spectrum of 1.0 M Pr^{3+} aqueous solution through four sheets of paper can be successfully measured by use of this spectrophotometer.[1] An acoustooptic tunable filter (AOTF) was used as the dispersive device in this spectrophotometer in order to provide all-solid-state nonmoving parts, high stability, and rapid scanning capability to the spectrophotometer.[2−4] As the AOTF can control and maintain the intensity of the light at a constant level (through the feedback loop),[5,6] this AOTF-EDFA spectrophotometer is very stable and has relatively low noise. Water in ethanol can be detected with this spectrophotometer at a limit of detection of 10 ppm.[1]

Compared to monochromators, the AOTFs have such advantages as compactness, all-solid-state construction, rapid scanning ability (microseconds), high diffraction efficiency (>90%) and resolution (e.g., 0.8 Å at 253.4 nm), and wide spectral tuning range. However, in spite of its compactness, the AOTF is not a fiber-based device.[2−6] As a consequence, advantages of fiber optics will not be fully realized if a fiber-based device such as EDFA is used together with the AOTF in a spectrophotometer. It is, therefore, important that a fiber-based AOTF be developed and synergistically used with the EDFA for the development of an all-fiber near-infrared spectrophotometer.

The availability of low-loss optical fibers has brought with it the need for integrated optical devices. To satisfy these demands, research in optics has entered into new areas in which integrations are among optical and acoustooptical components (integrated acoustooptics). 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 this theoretical and experimental work, integrated AOTFs (IAOTFs) have been developed.[7,8] These devices are based on the photoelastic effect, where surface acoustic waves (SAWs) diffract light from one polarization state to another.[7,8] Similar to bulk acoustooptic interaction, the polarization conversion is extremely wavelength specific. The required acoustic power is, however, substantially less than that of bulk devices because the SAWs can be confined in an acoustic waveguide. The scanning speed of the filter is relatively less (scan time less than 10 μs) than those of the bulk AOTFs (because of the shorter distance the acoustic wave has to travel in the IAOTF).[7,8] Furthermore, no optical

(1) Tran, C. D.; Gao, G. H. *Anal. Chem.* **1996**, *68*, 2264−2269.
(2) Tran, C. D. *Anal. Chem.* **1992**, *64*, 971A−981A.
(3) Tran, C. D.; Bartelt, M. *Rev. Sci. Instrum.* **1992**, *63*, 2932−2939.
(4) Lewis, E. N.; Treado, P. J.; Levin, I. W. *Appl. Spectrosc.* **1993**, *47*, 539−541.
(5) Tran, C. D.; Furlan, R. J. *Rev. Sci. Instrum.* **1994**, *65*, 309−314.
(6) Tran, C. D.; Furlan, R. *Appl. Spectrosc.* **1992**, *46*, 1092−1095.
(7) Heffner, B. L.; Smith, D. A.; Baran, J. E.; Yi-Yan, A.; Cheung, K. W. *Electron. Lett.* **1988**, *24*, 1562.
(8) Smith, D. A.; Johnson, J. J. *Electron. Lett.* **1991**, *27*, 2102.

S0003-2700(96)00919-5 CCC: $14.00

alignment is needed for the integrated AOTF because these devices capitalize on the ease of use of fiber-optically pigtailed units.

The information presented is, indeed, provocative and clearly indicates that it is possible to use the EDFA and IAOTF to develop a compact, portable, fast-scanning, all-fiber near-infrared spectrophotometer which requires no optical realignment and has high and very stable light throughput. Such considerations prompted us to initiate this study, which aims to characterize the IAOTF and use it together with the EDFA to develop an all-fiber near-infrared spectrophotometer. Additionally, application of this spectrophotometer will be investigated which aims not only to show the wide applicability of the EDFA but also to fully exploit its advantages. Specifically, we have previously reported[11] that the near-IR light emitted by the EDFA is particularly suited for the determination of trace chemicals that have O−H groups. In this paper, we will demonstrate that it is also suited for the determination of traces of gaseous samples that have N−H groups. This capability, together with the compact, all-fiber characteristic of the EDFA-IAOTF, makes this spectrophotometer particularly suited for leak detection of monomethylhydrazine, which is widely used as fuel for rockets and space shuttles. A preliminary report on the characterization of the IAOTF, instrumentation development of the EDFA-IAOTF near-infrared spectrophotometer, and its application will be given in this paper.

EXPERIMENTAL SECTION

The IAOTF used in this work was purchased from New Focus Corp. (Santa Clara, CA, Model 4511). This IAOTF was specified to have a center wavelength of 1550 nm and a tuning range larger than 80 nm (full width at half-maximum). The rf power required is less than 150 mW, which is much lower than those used for bulk AOTFs, which is in the order of a few watts.[1,9−11] This IAOTF is fusion-spliced directly to two single-mode optical fibers (one for input and the other for output). Each fiber is terminated with an FC/SPC connector to facilitate connection with other fiber-based components. Since this IAOTF is not of a noncollinear type but is rather a collinear configuration, polarizers are needed to provide polarized light for input and to separate diffracted light from transmitted light. To preserve the all-fiber characteristic of the IAOTF, fiber polarizers were used. These fiber polarizers were purchased from Sumitomo Osaka Cement Co. (Osaka, Japan). Essentially, there are single-mode fibers in which polarizing components were imbedded. Ends of these polarizing fibers are terminated with FC/SPC connectors.

The erbium-doped fiber amplifier (EDFA) used in this work is the same as that used previously.[1] The amplified spontaneous emission output from this EDFA was initially converted into linearly polarized light by means of the fiber polarizer before being introduced into the IAOTF. The second fiber polarizer was connected to the output of the IAOTF to remove the transmitted light and to transmit the diffracted light. The rf driver and amplifier, similar to those used previously,[1,9−11] were used to generate, amplify, and amplitude-modulate the rf signal for the IAOTF. Depending on the type of measurements, the spectrophotometer was used as a single beam or a double beam, i.e., sample and reference beam. The latter was accomplished by means of a beamsplitter to split the light into the reference and the sample beams. Intensity of the light was detected by thermoelectrically cooled InGaAs detector(s) (Electro-Optical Systems Model IGA-020HS-E). The output signal(s), which was AM modulated, was connected to lock-in amplifier(s) (Stanford Research Systems Model SR 810) for demodulating and amplifying. The signal(s) from the lock-in-amplifier(s) was then connected to a microcomputer through a 16-bit A/D interface board (National Instruments Model AT MIO 16X).

Diethylamine, triethylamine, and monomethylhydrazine were purchased from Aldrich Chemical Co. and used as received. Gas phase samples were prepared by placing two or three drops (about 10−15 μL) of the liquid sample into a closed cylindrical cuvette having 10-cm path length and 2.0-cm diameter. Vapor pressures of samples were estimated on the basis of the temperature of the cell and the known partial pressures.[12]

RESULTS AND DISCUSSION

Because of the long interaction length between the SAWs and the light, it is expected that the resolution of this IAOTF is much better than those of the corresponding bulk AOTFs. It was determined by the manufacture, through indirect measurement of applied rf frequency, that the resolution of this IAOTF is less than 2 nm (at 3-dB filter width, i.e., full width at half-maximum). An experiment was designed to directly determine the resolution of this IAOTF. In this experiment, a single-mode (single-frequency) erbium fiber laser was used as the light source. Shown in Figure 1A is the output spectrum of this fiber laser measured by an optical spectrum analyzer. As illustrated, the laser provides single-frequency output light at 1554.010 nm, with a bandwidth of less than 0.10 nm. The spectrum of the diffracted light, obtained when this fiber laser was connected to the IAOTF, is shown in Figure 1B. It can be calculated from this spectrum that the resolution (i.e., full width at half-maximum) of this IAOTF is about 1.7 nm. This is about 10 times narrower than those for bulk AOTFs in the same region, which are in the order of 8−15 nm.[1,11] It is noteworthy that the side peak at 1551.50 nm is not due to the fiber laser but is rather due to the side lobes of the IAOTF.

This single-frequency fiber laser also facilitated the determination of the diffraction efficiency of the IAOTF. This was accomplished by measuring the ratio of the intensities of the diffracted linearly polarized light (from the IAOTF) and of the input linearly polarized light (by the fiber polarizer) from the fiber laser. The diffraction efficiency at 1554.01 nm was determined to be 37 ± 3%. This efficiency is much higher than those of corresponding (bulk) collinear AOTFs. In fact, as reported previously by us, a collinear (bulk) AOTF for the UV and visible region has efficiency only in the 10−14% range.[9] Furthermore, up to 5 W of rf power was used on this bulk AOTF[9] in order to achieve this efficiency, whereas the power required for the IAOTF is about 33 times lower (i.e., 150 mW). The ability to provide high diffraction efficiency at much lower rf power makes this IAOTF particularly advantageous for the construction of a near-infrared spectrophotometer because it offers not only a compact size but also higher light throughput with lower noise.

Absorption spectra of air saturated with vapor of diethylamine and triethylamine in a 10-cm-path length cell, measured with this EDFA-IAOTF near-infrared spectrometer for the region from 1505

(9) Tran, C. D.; Lu, J. *Anal. Chim. Acta* **1995**, *314*, 57−66.
(10) Pasquini, C.; Lu, J.; Tran, C. D.; Smirnov, S. *Anal. Chim. Acta* **1995**, *319*, 315−324.
(11) Baptista, M. S.; Tran, C. D.; Gao, G. H. *Anal. Chem.* **1996**, *68*, 971−976.
(12) Schmidt, E. W. *Hydrazine and its Derivatives*; John Wiley: New York, 1984.

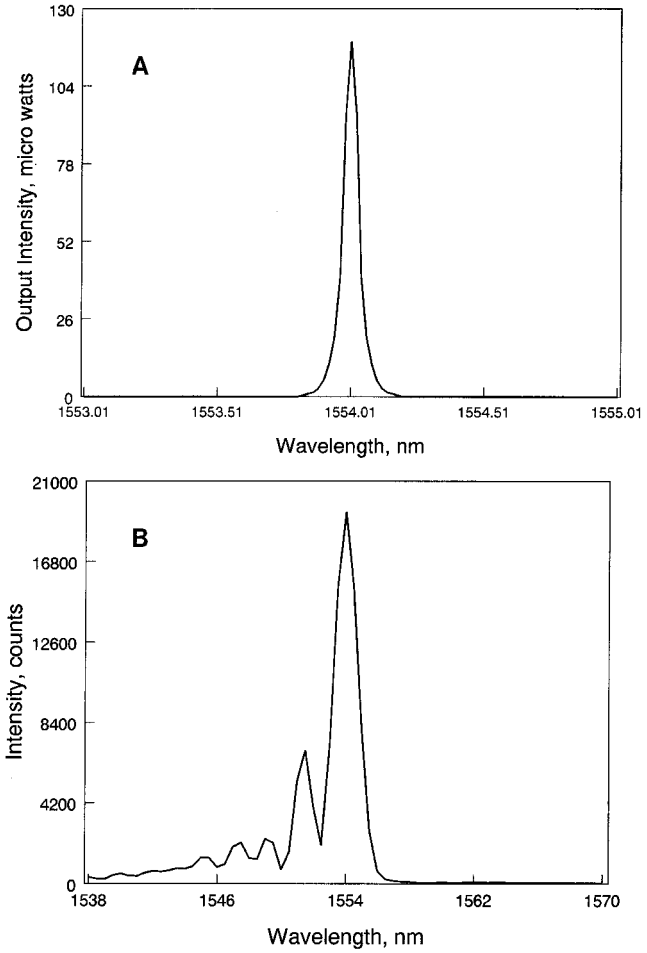

Figure 1. Spectral output of the single-frequency erbium fiber laser measured with (A) optical spectrum analyzer and (B) integrated acoustooptic tunable filter.

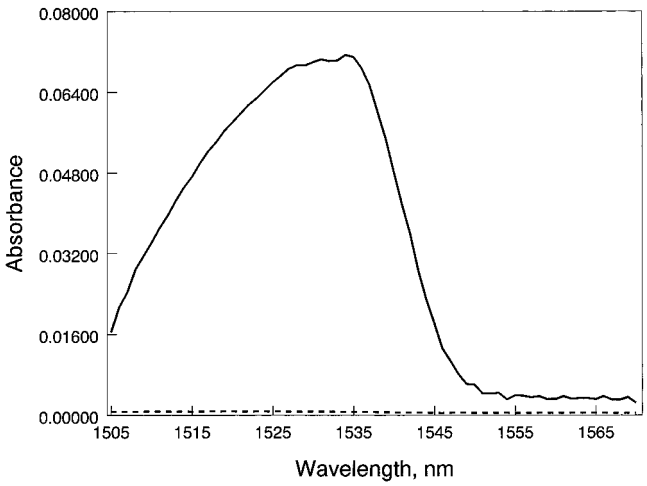

Figure 2. Absorption spectra of air saturated with vapor of diethylamine (—) and triethylamine (- - -) in a 10-cm cell, measured with the IAOTF-EDFA near-infrared spectrophotometer.

to 1570 nm, are shown in Figure 2. As illustrated, triethylamine exhibits no absorption, whereas diethylamine shows a strong absorption band at 1534 nm. This is as expected because this band is due to the first overtone of the N−H stretching.

The ability to detect an overtone of the N−H group makes this spectrometer suited for the detection of monomethylhydrazine (MMH), which is widely used as fuel for rockets and space shuttles. The absorption spectrum of MMH vapor in the region

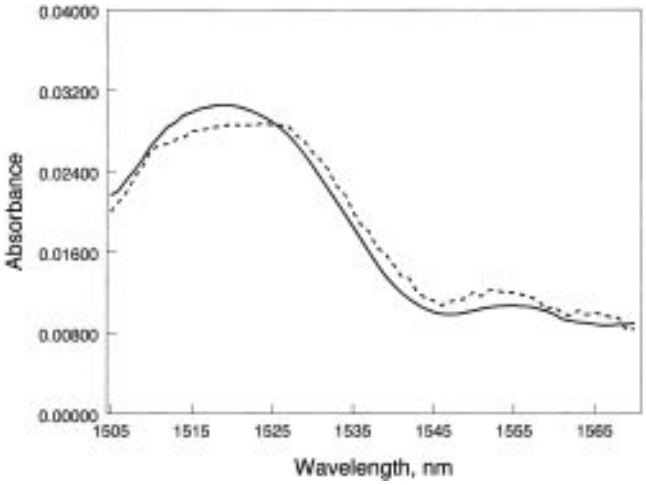

Figure 3. Absorption spectra of air saturated with vapor of monomethylhydrazine in a 10-cm cell, taken on the IAOTF-EDFA near-infrared spectrophotometer without (—) and with one sheet of paper (- - -).

from 1505 to 1570 nm, measured using this spectrophotometer, is shown in Figure 3. As illustrated, MMH exhibits two peaks in this region: a major peak at 1519 nm and a small one at 1555 nm. These are in agreement with spectra reported previously and hence can be assigned to the $\Delta\nu = 2$ overtones of the N−H stretching fundamentals ν_1 and ν_2 at 3317 and 3245 cm^{-1}, respectively.[13]

Assuming that equilibrium is reached between two drops of MMH and the air inside the cell, the vapor pressure of the MMH inside the cell can be calculated by using

$$\log P\ (\text{mmHg}) = 7.11158 - \frac{1104.5711}{T} - \frac{152227.7}{T^2}$$

where T is the absolute temperature.[12] As the temperature of the cell was at 25 °C, the vapor pressure of MMH inside the cell was calculated to be 50 Torr. The corresponding absorbance for this concentration, as illustrated in Figure 3, is 0.031. The limit of detection of this all-fiber-based near-IR instrument was determined to be 90 μAU, which is comparable with those found for the lamp-based[11] and EDFA-based[1] (bulk) AOTF near-infrared spectrophotometers developed in our laboratory. Accordingly, the minimum amount of MMH vapor in air that can be determined (in a 10-cm-path length cell) by this EDFA-IAOTF near-infrared spectrophotometer is estimated to be about 191 ppm. It is true that this LOD value is somewhat higher than the values obtained using FT-IR instruments.[12] However, this near-IR spectrophotometer possesses several advantages that make it particularly desirable. Specifically, in this case, the MMH vapor is measured in the near-IR region. There is no need for special sample preparation. The cell path length is only 10 cm, which is much shorter than the multiple path length cells used in FT-IR (e.g., 666 cm as used in ref 13). Furthermore, the compact, all-fiber characteristic of this EDFA-IAOTF-based instrument makes it possible to perform the measurement directly on-line and in real time. This is of particular importance considering the origin of the MMH vapor that needs to be measured, e.g., to determine the leak of fuel in rockets and space shuttles.

(13) Murray, M.; Kurtz, J. *J. Quant. Spectrosc. Radiat. Transfer* **1993**, *50*, 585−590.

An experiment was also designed to demonstrate the high-throughput characteristic of this spectrometer. Shown as a dashed line in Figure 3 is the absorption spectrum of the same 50 Torr air-saturated sample of monoethylhydrazine measured by placing the sample behind a sheet of photocopy paper (Cascade X-9000 white paper). The intensity of the EDFA is so high that, after passing through the paper, enough light was transmitted to facilitate the absorption measurement of the sample. As expected, the absorption spectrum measured with the paper agrees well with that measured without the paper (in the figure, the absorption of the paper was used as a baseline to facilitate the comparison of two measurements). Relatively higher noise, however, was found when the paper was present. Scattering of light by the paper, which in turn reduces the amount of light reaching the detector, is presumably responsible for the observed noise increased.

In summary, we have successfully demonstrated that advantages of the integrated AOTF over the (bulk) AOTFs include all-fiber construction, smaller size, narrower spectral resolution, higher diffraction efficiency, and lower rf power requirement. A relatively narrow spectral tuning range (about 80 nm) is the only drawback for this integrated tunable filter. However, this disadvantage can be easily 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, we have demonstrated that an all-fiber, compact, high-throughput near-infrared spectrophotometer can be successfully constructed by synergistic use of this integrated AOTF and the EDFA which has been shown to provide high intensity and wide spectral bandwidth in the infrared region from 1500 to 1600 nm. This spectral region is particularly useful for the determination of samples that have O−H and/or N−H groups. The all-fiber nature, compactness, high throughput, and high sensitivity of this spectrometer make it particularly suitable for the on-line and real-time detection of trace gases in hostile environments, including leak detection of monomethylhydrazine, which is often used as the hypergolic propellant for the space shuttle thruster systems.

Acknowledgment is made to the National Institutes of Health, National Center for Research Resources, Biomedical Research Technology Program for financial support of this work.

Received for review September 11, 1996. Accepted January 10, 1997.[⊗]

AC960919U

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1997.