

# Near-Infrared Detection of Flow Injection Analysis by Acoustooptic Tunable Filter-Based Spectrophotometry

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**The instrumentation development of a near-infrared (near-IR) spectrophotometer based on an acoustooptic tunable filter (AOTF) and its application as a detector for flow injection analysis (FIA) are reported. In addition to being compact and all solid state, this AOTF-based instrument is very sensitive, has high resolution, and can be rapidly scanned. The latter advantage make it uniquely suited as a detector for FIA, in that it can rapidly record the whole near-IR absorption spectrum of a mixture passing through the FIA flow cell. Subsequent treatment of the recorded spectra with multivariate calibration methods makes it possible to use the FIA, for the first time, for such applications as the simultaneous determination of trace amounts of water and benzene in ethanol. Because all organic compounds absorb light in the near-infrared region, this AOTF-based near-IR detector can serve as a universal detector for FIA; as a consequence, applications of the FIA techniques can be expanded to other areas which are not possible otherwise.**

Flow injection analysis (FIA) is among the most widely used methods for automated analysis. Its application to several fields of chemistry has been demonstrated in recent years.<sup>1,2</sup> Several operational modes of FIA have been realized by appropriately modifying traditional wet chemical methods (dilution, extraction, titration, fast kinetic reactions, dialyses) for use in automated flow devices.<sup>1–8</sup> Different types of detectors, including electrochemical, spectrophotometric, and luminescent, have been applied to FIA.<sup>1,2</sup> While these detectors have been shown to be effective, they can only be used for certain types of compounds. Relatively wider applicability can be achieved with detectors based on measurements of the refractive index, or rather the refractive index gradient.<sup>9–11</sup> Unfortunately, the sensitivity of this type of detectors

is rather low. There has not been a FIA detector that not only is universal but also has high sensitivity and selectivity.

Spectrochemical applications of the near-infrared (near-IR) absorption technique have increased significantly in recent years.<sup>12–16</sup> Several reasons account for the popularity, including the wide applicability (all compounds that have C–H, O–H, or N–H absorb 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.<sup>16</sup> These features enable the near-IR to serve as a universal detector for FIA. However, the detection of FIA by near-IR has not been fully explored. In fact, there are only two reports describing the utilization of near-IR for continuous-flow FIA detection.<sup>17,18</sup> Unfortunately, in these studies, the potentials of the near-IR technique have not been fully exploited because they were based on the use of only a single wavelength. As a consequence, the multivariate calibration methods cannot be used to analyze data in these studies.<sup>17,18</sup>

Most near-IR spectrophotometers are based on grating monochromators. Because of the low scanning speed of these devices, it is not possible to measure whole near-IR spectral regions in the time frame necessary for FIA determinations. Faster scanning can, in principle, be achieved with the use of a photodiode array detector (PDA). Since silicone-based detectors can only respond up to about 1100 nm, a PDA for the near-IR has to be based on novel materials, such as InGaAs. In fact, InGaAs-based PDA has been developed recently and proved to be effective for the near-IR region.<sup>19</sup> However, because of the high cost, the use of the InGaAs-based PDA for routine online analyses has not been realized. An acoustooptic tunable filter (AOTF) offers a solution to these problems. AOTF is an all-solid-state, electronic dispersive device based on the diffraction of light by an acoustic wave in an anisotropic crystal. The wavelength of the diffracted light is dependent of the frequency of the acoustic wave; i.e., only a monochromatic light will be diffracted from a crystal when a specific acoustic wave propagates through it. The scanning speed

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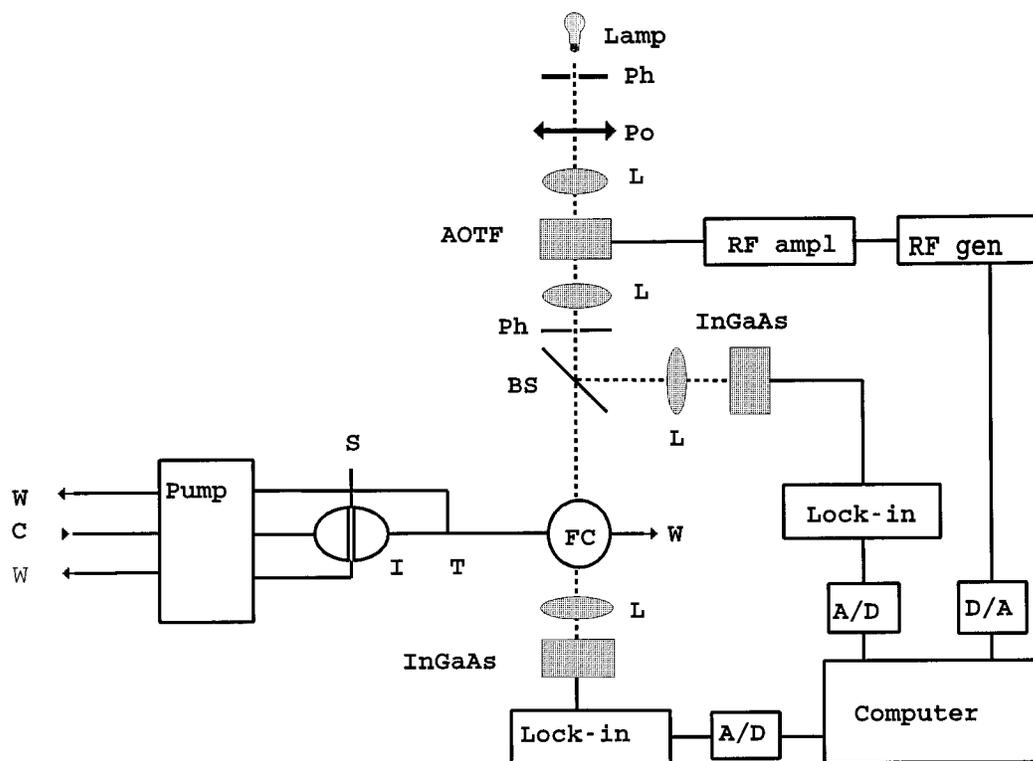


Figure 1. Near-IR-FIA instrument: W, waste; C, carrier; Pump, peristaltic pump; S, sample; I, injector; T, T connector; FC, flow cell; Ph, pinhole; Po, polarizer; L, lens; BS, beamsplitter.

of the AOTF 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 (i.e., contains no moving parts), having rapid scanning ability ( $\mu\text{s}$ ), allowing high-speed random or sequential wavelength access, giving high resolution (a few angstroms), and having a wide spectral tuning range.<sup>20–22</sup> In fact, AOTF has been called “the new generation monochromator” and has provided a unique means for the development of novel instruments which are not possible otherwise.

The information presented is, indeed, provocative and clearly indicates that an AOTF-based near-infrared spectrophotometer, which has the combined advantages of the near-IR technique and the AOTF, should serve as a sensitive and universal detector for FIA. Such considerations prompted us to initiate this study, which aims to develop this type of spectrophotometer and demonstrate its applicability as a detector for FIA. In this paper, the instrumentation development of the detector is reported. Subsequently, the performance of the detector is evaluated by using it in two different measurements, i.e., determination of trace amounts of water in chloroform and water and benzene in ethanol.

## EXPERIMENTAL SECTION

**Materials.** Deionized water was distilled in an all-glass apparatus. Chloroform was purchased from Aldrich (HPLC grade). **Note:** Chloroform is highly toxic and is a cancer suspect agent. Absolute ethanol was purchased from Aaper Alcohol and Chemical Co. The Karl-Fischer method was used to determine the concentrations of water in these solvents. They were found

to be  $0.07 \pm 0.01\%$  (v/v) (for ethanol) and  $<0.008\%$  (v/v) (for chloroform). Benzene (Aldrich) was distilled from sodium and benzophenone. All solvents were sonicated for 30 min prior to use.

**Instrumentation.** The instrument utilized consists of a single line manifold flow injection device. As can be seen in Figure 1, a peristaltic pump (Gilson Minipuls 2), operating at a flow rate of 1.6 mL/min, was used to pump solvent and sample through the sample injector (home-made of Teflon, 108  $\mu\text{L}$  sample volume) and then to the flow cell. Two home-made flow cells were used. They were made of Teflon, having path lengths of 1.7 and 0.75 cm and diameters of 3 and 4 mm, respectively. A T connector was placed between the injection valve and the detector to generate a new channel in order to facilitate the trapping and removal of air bubbles. This particular channel was used only when it was necessary to remove trapped air bubbles. The detector was a home-built near-IR spectrophotometer. In this spectrophotometer, a 100-W, 12-V halogen tungsten lamp (Osram 64623) was used as the light source. The collimated incident white light from the light source was dispersed to monochromatic light and spectrally scanned by means of a noncollinear AOTF (Matsushita Electronics Model EFL-F20R2), which was fabricated from  $\text{TeO}_2$ . A driver constructed from a voltage control oscillator<sup>20–22</sup> provided the radio frequency (rf) signal. The rf signal from this driver was amplitude-modulated at 50 kHz by a home-built modulator and amplified by a rf power amplifier (Mini-Circuits Model ZHL 1-2W) prior to being applied to the AOTF. The light diffracted from the AOTF was split into two beams (i.e., sample and reference) by means of a beamsplitter. The flow cell was placed in the sample beam. The intensity of the light in the sample and reference beams was detected by thermoelectrically cooled InGaAs detectors (Electro Optical Systems Model IGA-

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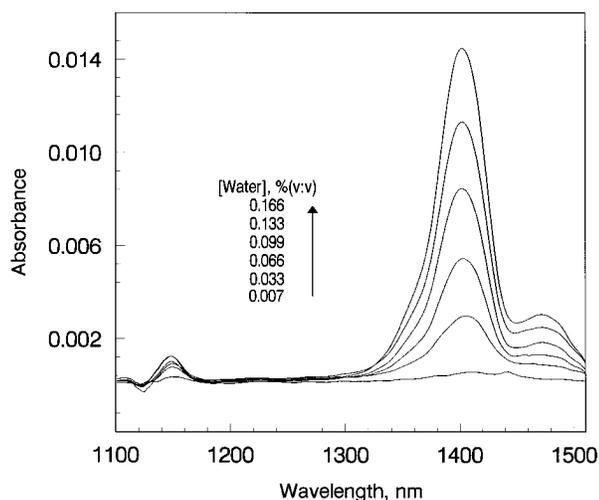


Figure 2. Near-IR spectra of chloroform solutions containing different concentrations of water, measured with a 1-cm quartz cuvette (blank solution is pure chloroform).

020HS-E). The output signals from the detectors, which were AM modulated at 50 kHz, were connected to lock-in amplifiers (Stanford Research Systems Model SR 810) for demodulation and amplification. The signals from the lock-in amplifiers were then connected to a microcomputer (Gateway 2000 DX2, 50 MHz) through a 16-bit A/D interface board (National Instruments Model AT MIO 16X). Software written in C++ language was used to control the frequency and the power and to scan the applied rf signal. The same software also facilitated the data acquisition and analysis (e.g., calculation of the absorption spectra) and was used to save the data in ASCII format for subsequent data treatment using other software packages (e.g., Gram-386 and Slide-Write). An optical switch was used to synchronize the introduction of the sample solutions into the FIA manifold and the start of the data acquisition. All reported spectra are averages of either three or four spectra. No other spectral pretreatment (smoothing, noise reduction) was employed.

## RESULTS AND DISCUSSION

The effectiveness of the near-IR spectra for determinations of purity of solvents is initially investigated by measuring near-IR spectra of various solvents in 1-cm cuvettes without flow. Upon confirmation, the near-IR spectrophotometer will be used as the detector for flow injection analysis to determine the purity of those solvents.

**(1) Determination of Water in Chloroform.** Shown in Figure 2 are the near-IR spectra of several chloroform solutions containing different concentrations of water (pure chloroform was used as blank). Several features are evident from the figure. Increasing the concentration of water leads to a relatively large increase in the absorption in the 1300–1500-nm region, a small increase at 1150 nm, and an even smaller decrease in absorption at 1125 nm. The observed increases in both regions can be attributed to the O–H group, namely the first overtone transition at 1450 nm and the combination of stretching and bending at 1180 nm.<sup>23–25</sup> There seem to be two bands in the 1300–1500-nm

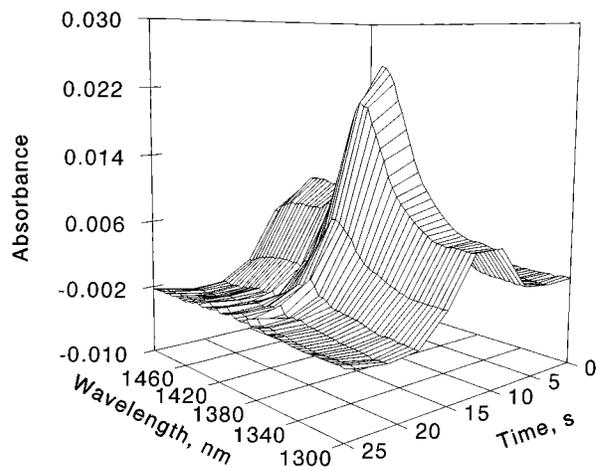


Figure 3. Absorption as a function of time and wavelength after the injection of 0.10% (v/v) water solution in chloroform (absorption spectra measured with a 1.7-cm flow cell).

region: one centered at 1400 nm and the other at 1450 nm. However, the presence of these two bands as well as the shoulder between them is probably not related to the presence of different absorbing species in solution or of different transitions of the water molecule. Rather, it is probably caused by the stretching and bending combination transition of the C–H group ( $\lambda_{\text{max}} = 1410$  nm).<sup>24</sup> Because adding water leads to a decrease in the concentration of chloroform, absorption of the C–H band will decrease as the concentration of water increases. The combination of these effects (i.e., the increase in the O–H band and the decrease in the C–H band) results in the spectral shapes observed for the 1300–1500-nm region. The presence of the negative absorption observed at 1125 nm can be explained using the same rationalization. In this case, there is also a decrease in the C–H absorption in the 1125-nm region because of a decrease in the chloroform concentration concomitant with the increase in the water concentration.

The absorption values measured in the spectral region from 1300 to 1500 nm were found to be correlated with the concentration of water present in the sample. A calibration model based on the partial least-squares (PLS) method was developed, using the spectral region (SR) from 1350 to 1500 nm (number of factors (NF) equal to 1). Very good correlation was found between the added and the calculated concentrations of water ( $r = 0.999$ ), with a root mean square deviation (RMSD) of 0.002%. The limit of detection (LOD), defined as two times the blank standard deviation divided by the sensitivity, was calculated to be 18 ppm ( $\mu\text{L/L}$ ) of water (based on the data at 1404 nm).

The determination of water in chloroform was then applied to the flow injection analysis using a flow cell having a 1.7-cm path length. Again, pure chloroform was used to obtain the blank signal. Chloroform samples with different concentrations of water from 0.01 to 0.10% (v/v) were injected in the flow of pure chloroform. Each sample was injected three times.

Shown in Figure 3 is the FIA absorption peak profile (i.e., absorption spectrum as a function of time) obtained when a solution of 0.10% (v/v) water was injected into the chloroform carrier. 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 absorption reaches its maximum 12 s after the injection and then starts to decrease. As expected, the changes of the absorption against wavelength and the

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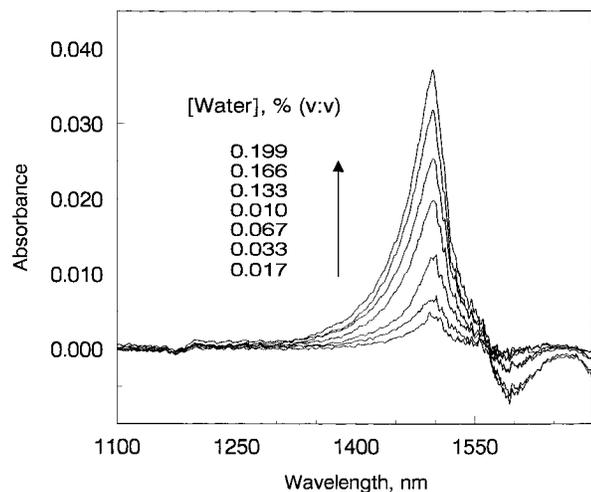


Figure 4. Absorption spectra of ethanol solutions containing different concentrations of water, measured with a 1-cm quartz cuvette (blank solution is pure ethanol).

concentration of water, measured in the FIA instrument, are the same as those observed for the solutions measured in the 1-cm cuvette without flow (Figure 2). Using the spectra measured 12 s after the injection for different concentrations of water, a calibration model based on the PLS method was developed for the determination of water in chloroform, using the spectral region from 1378 to 1424 nm ( $NF = 1$ ). Good correlation was obtained between the concentration of water injected and the concentration of water calculated by the model ( $r = 0.997$ ). The RMSD for this determination was calculated to be 0.002%. The LOD at 1400 nm was found to be 13 ppm ( $\mu\text{L/L}$ ) of water. This LOD value is smaller than the value calculated for the assay using a nonflowing 1-cm cuvette (i.e., 18 ppm, Figure 2). Although the blank noise in the flowing experiment is larger, the sensitivity obtained was also higher, due to the fact that the flow cell has a longer path length (1.7 cm). This explains the relatively smaller LOD value calculated in the FIA experiment.

**(2) Determination of Water and Benzene in Ethanol.** The determination of water and benzene in ethanol is of industrial importance because benzene is often added to ethanol to facilitate the removal of its water impurity by distillation. This type of measurement is relatively more complex than the previous experiment (i.e., the determination of water in chloroform) because it involves the determination of two components. Furthermore, ethanol has a much higher background absorption compared to that of chloroform.

The changes in the absorption spectra observed upon the addition of water to ethanol are shown in Figure 4 (absorption measured in a 1-cm quartz cell without flow and with pure ethanol as blank). As can be seen (Figure 4), there is an increase in the absorption in the 1300–1550-nm region. This is, as explained previously, related to the presence of the first O–H overtone transition. This O–H transition is supposedly different for water and ethanol in terms of both frequency and oscillator strength. For example, the  $\lambda_{\text{max}}$  values of the O–H first overtone band for  $\text{H}_2\text{O}$  and ethanol were reported to be 1450 and 1550 nm, respectively.<sup>23,24</sup> Using PLS, a calibration model for the determination of water in ethanol was developed ( $SR = 1370\text{--}1537$  nm,  $NF = 2$ ). There is good correlation between the added and calculated concentrations of water in ethanol ( $r = 0.997$ , RMSD

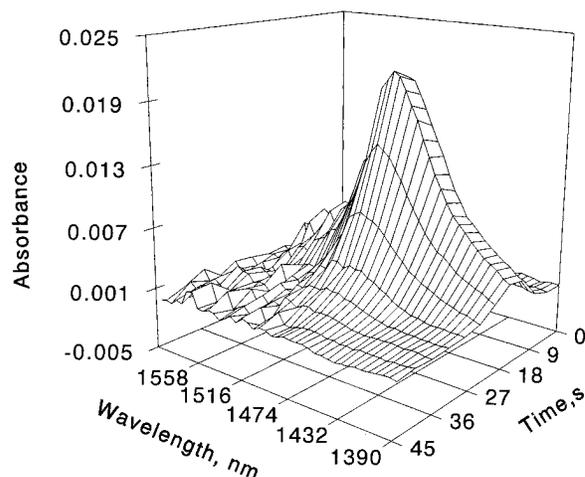


Figure 5. Absorption as a function of time and wavelength after the injection of 0.45% (v/v) water solution in ethanol (absorption spectra measured with a 0.75-cm flow cell).

= 0.004%). The LOD for this determination was calculated to be 10 ppm at 1497 nm.

The determination of dryness of ethanol was also tried in the FIA instrument using a 0.75-cm optical path flow cell. The 1.7-cm-path length flow cell used for the determination of water in chloroform is not suitable for this measurement, because the absorption of ethanol in this region is much larger than that of chloroform. As a consequence, the light intensity reaching the detector was very small when the 1.7-cm cell was used. Furthermore, the effects of the refractive index gradients that were generated in the determinations of benzene and water in ethanol were much smaller in the case of the 0.75-cm-path length flow cell than in the 1.7-cm flow cell. Again, pure ethanol was used as blank, and ethanol samples with different concentrations of water (from 0.09% to 0.45%) were injected into the near-IR–FIA instrument. Each measurement was performed at least four times.

Shown in Figure 5 is the FIA absorption peak profile obtained when a 0.45% (v/v) water solution was injected into the ethanol flow carrier. It is evident that, as the concentration of water increases inside the flow cell, there is an increase in the absorption from 1390 to 1550 nm, similar to the effect observed for the experiment performed without flow (Figure 4). The concentration of water inside the flow cell increases from 0 to 12 s, where it reaches its maximum and remains relatively constant up to 16 s, after which it starts to decrease. Using the spectra measured 16 s after the injection of samples with different concentrations of water, a calibration model based on the PLS method was developed for this determination ( $SR = 1400\text{--}1520$  nm,  $NF = 2$ ). Good correlation was obtained between the injected and the calculated concentrations of water ( $r = 0.999$ ). The RMSD for this determination was calculated to be 0.006%. The LOD for the near-IR–FIA detection of water in ethanol was determined to be 80 ppm at 1494 nm.

Figure 6 shows the changes in the absorption spectra observed upon adding benzene to ethanol (1-cm nonflowing cell). Several features are evident. Namely, with the increase in benzene concentration, there is a relatively large increase in the 1650–1700-nm region, a decrease in the 1500–1650-nm region, a smaller decrease in the 1160–1250-nm region, and a small increase in the 1100–1160-nm region. The increase observed in the 1650–1700-nm region is probably related to the presence of the first

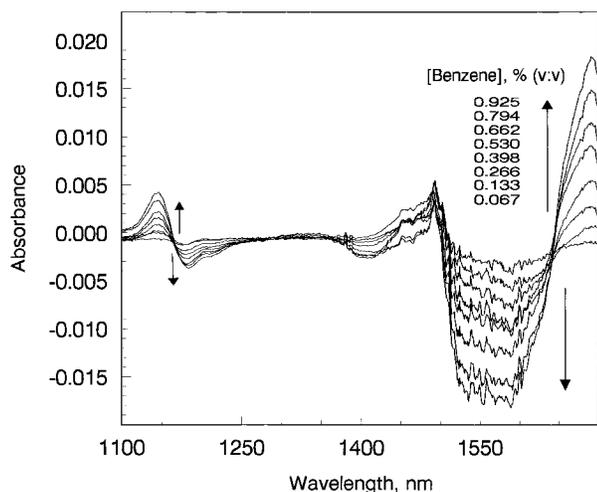


Figure 6. Absorption spectra of ethanol solutions with different concentrations of benzene. Spectra were measured in a 1-cm cuvette using ethanol as blank.

overtone stretching transition of the C–H groups (of benzene) around 1675 nm. This transition is at a different wavelength than that observed for the same type of transition of the C–H groups of ethanol (this transition in ethanol is located around 1700 nm).<sup>24</sup> The decreases observed in the 1160–1250- and 1500–1650-nm regions can be explained by the decrease in the concentration of ethanol and, consequently, in its absorption in these regions (with the increase in the concentration of benzene). The small increase observed in the 1100–1160-nm region is probably related to the second overtone C–H transition of benzene, located around 1143 nm.<sup>24</sup> All these regions can be used to develop a PLS-based calibration model for the determination of benzene in ethanol (SR = 1187–1219, 1526–1579, and 1660–1697 nm, NF = 4). Good correlation was obtained between the added and calculated concentrations of benzene ( $r = 0.999$ , RMSD = 0.008%). The LOD for the determination of benzene in ethanol was calculated to be 51 ppm at 1692 nm.

The determination of benzene in ethanol was then performed using the FIA instrument with a 0.75-cm-path length flow cell. Again, pure ethanol was used as blank, and samples with different concentrations of benzene (from 0.11% to 1.6%) were injected into the near-IR–FIA instrument. Each measurement was performed at least four times.

Shown in Figure 7 is the FIA absorption peak profile obtained when a 1.6% (v/v) benzene solution was injected into the ethanol flow carrier. It is evident that, as the concentration of benzene increases inside the flow cell, there is an increase in the region from 1650 to 1700 nm and a decrease in the 1500–1650-nm region. As expected, this observation is similar to that for the same type of measurements performed without flow (Figure 6). Using the spectra measured 12 s after the injection, a calibration model based on the PLS method was developed for this determination (SR = 1511–1598 and 1657–1700 nm, NF = 1). Good correlation was obtained between the concentration of benzene injected and the concentration of benzene calculated by the model ( $r = 0.999$ ). The RMSD and LOD (1700 nm) for this determination were calculated to be 0.018% and 124 ppm, respectively.

To simultaneously determine the concentrations of benzene and water in ethanol, the near-IR spectra of 22 samples containing different concentrations of benzene and water were measured in a nonflowing 1-cm cell. For clarity, only some of the spectra are

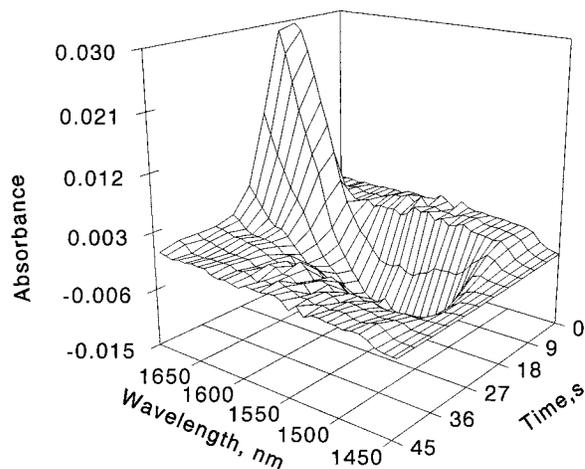


Figure 7. Absorption as a function of time and wavelength after the injection of 1.6% (v/v) benzene solution in ethanol (absorption spectra measured with a 0.75-cm flow cell).

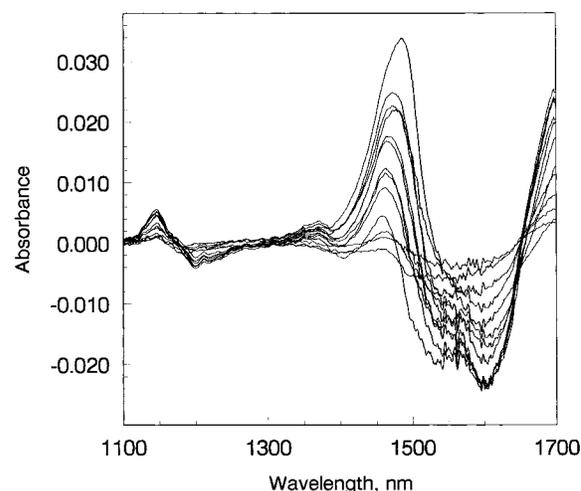


Figure 8. Near-IR absorption spectra (1-cm cuvette using ethanol as blank) of ethanol solutions containing different concentrations of water [from 0.07% to 0.23% (v/v)] and benzene [from 0.1% to 0.87% (v/v)].

shown in Figure 8. As illustrated, the spectrum of an ethanol solution containing a mixture of water and benzene has spectral features that are similar to those obtained by adding the spectra of the corresponding components (i.e., water and benzene). Specifically, the increase in the concentration of benzene caused an increase in the 1650–1700- and 1100–1160-nm regions and a decrease in the 1500–1650- and 1160–1250-nm regions. The increase in the concentration of water caused an increase in the 1400–1550-nm region. However, both components do interfere with each other, especially around the 1500-nm region, where water caused an increase in the absorption band but benzene decreased it. A calibration model based on the PLS method was developed for the simultaneous determination of the concentrations of water and benzene (SR = 1471–1486, 1679–1695, 1189–1197, and 1555–1580 nm, NF = 4 and 5 for water and benzene, respectively). Good correlation was found between the added and calculated concentrations of water ( $r = 0.994$ , RMSD = 0.0088%). The concentration of benzene can also be accurately obtained from this model. The correlation coefficient and RMSD were found to be 0.999 and 0.0086%, respectively.

It is clear from the above results that it is possible to sensitively and simultaneously determine the concentrations of water and

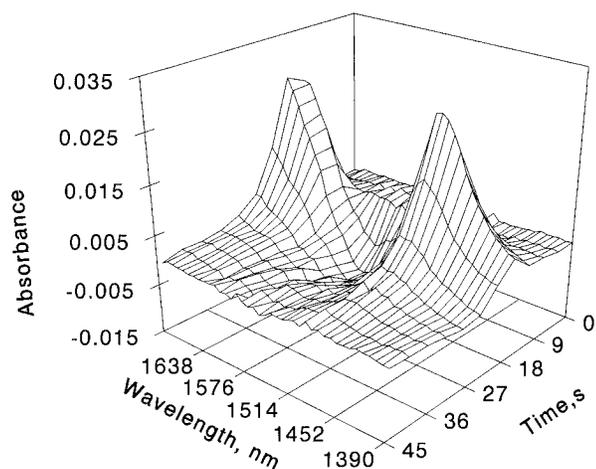


Figure 9. Absorption (0.75-cm flow cell using ethanol as blank) as a function of time and wavelength measured after the injection of ethanol solution containing 0.6% and 1.5% (v/v) of water and benzene, respectively.

benzene in ethanol by near-IR spectrometry. Therefore, the next step is to perform this determination in the near-IR-FIA instrument. Figure 9 shows the absorption measured as a function of time and wavelength after the injection of sample 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 and 26 s, there is an increase in the absorption in the 1650–1700- 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). These spectral profiles are the same to those observed in the previous measurements using the nonflowing 1-cm cuvette (Figure 8). To produce a calibration model for the simultaneous determination of benzene and water in ethanol using the near-IR-FIA technique, 21 samples containing different concentrations of water and benzene were prepared. Each sample was injected four times. Good correlation was obtained between the concentration of water and benzene injected and the concentration of both components calculated by the PLS model (SR = 1450–1496, 1672–1700, and 1583–1602 nm, NF = 4 and 3 for water and benzene, respectively). The statistical parameters obtained were  $r = 0.997$ , RMSD = 0.015% and  $r = 0.997$ , RMSD = 0.033% for water and benzene, respectively.

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## CONCLUSION

We have shown in this report the first development and applications of an AOTF-based near-IR spectrophotometer as a detector for FIA. Because of the high scanning velocity and wavelength accuracy that can be obtained with this AOTF-based instrument, the whole near-IR spectral region was obtained 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. In fact, 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 a two-component system (i.e., the concentrations of water and benzene in ethanol). For simple one-component systems, the LOD of this AOTF-near-IR-FIA technique is comparable to that obtained with FIA spectrophotometry<sup>25</sup> as well as to that with the single-wavelength near-IR-FIA technique.<sup>17,18</sup> In this case, the advantages of the AOTF-near-IR-FIA instrumentation are its sensitivity, automation, and wide applicability.

For relatively more complex systems (e.g., two-component systems), the advantages become more prevalent. While it is true that a refractive index detector can be used with FIA for the simultaneous determination of multicomponent samples, the sensitivity of this type of detector is rather low, and it is not molecular specific.<sup>26</sup> In fact, there is not a method currently available that can be easily coupled with an FIA instrument for the sensitive and simultaneous determination of the concentrations of two or more components without sample pretreatment. The present automated and real-time determination of water and benzene in ethanol is important because ethanol is increasingly being used as a substitute for or an additive to gasoline (i.e., it is important to know the concentrations of water and benzene impurities in such systems).

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