



STUDY OF NEAR INFRARED ABSORPTION SPECTROSCOPY OF SELECTED PAIRS OF ORGANIC SOLVENTS FOR QUALITY CONTROL APPLICATIONS

M. USMAN¹, *S. A. JANJUA², M. A. ALEEM² and M. J. HYDER¹

¹Pakistan Institute of Engineering and Applied Sciences (PIEAS), P.O. Nilore, Islamabad, Pakistan

²Accelerator and Carbon Based Nanotechnology Laboratory, Physics Division, PINSTECH, P.O. Nilore, Islamabad, Pakistan

(Received October 26, 2010 and accepted in revised form December 07, 2010)

Organic solvents of various combinations & ratios, such as ethanol/commercial petrol; benzene/ethanol; toluene/commercial petrol and toluene/benzene were studied by near infrared (NIR) absorption spectroscopy. NIR spectrometer of 850–1700 nm produced distinctly separable spectral ranges for all the combinations; 1400 to 1650 nm for ethanol/commercial petrol; 1125 to 1150 nm for benzene/ethanol; 1130 to 1150 nm for toluene/commercial petrol and 1175 to 1210 nm for toluene/benzene. The calibration curves were drawn for the given pair concentrations. From the linear fitting parameters it is evident that each pair has different slope, which establishes reliability of the technique. The results revealed that each solvent in the mixture gives a clear trend of spectral region. This may be used for the analysis of mixtures of organic solvents. The technique may be utilized for the quality assurance.

Keywords: NIR absorption spectroscopy, Ethanol, Petrol, Benzene, Quality control.

1. Introduction

Infrared spectroscopy is one of the most common spectroscopic techniques used in many industrial, environmental, medical, food processing and security applications. Although NIR spectral range is very narrow part of the whole IR but is still very useful for many applications. Workman and Weyer [1] explored NIR applications and thoroughly discussed the spectra of several compounds including bromoform, chloroform, methylene chloride, benzene, methanol, and m-toluidine. They cited potential of the spectral region to the analysis of mixtures of organic compounds, water in hydrocarbons and other solvents such as alcohols, acids, amines, benzene and olefins in the same milieu. Lee et al. [2] discussed the importance of spectral range optimization for the NIR quantitative analysis of petrochemical and petroleum products such as naphtha and gasoline, which results in improved calibration performance. NIR spectroscopy was used by Balabin et al. [3-6] to compare six different calibration models (multiple linear regression, principal component regression, linear partial least squares regression, polynomial partial least

squares regression, spline partial least squares regression and artificial neural networks (ANN) for gasoline properties prediction and found ANN to be the most suitable calibration model. They obtained quantitative data of ethanol-gasoline distribution over fractions of ethanol-gasoline fuel. Ethanol is found to distribute itself nonuniformly among gasoline fractions. It is concentrated in "light" ethanol-gasoline fractions and is almost completely absent in "heavy" ones (with a boiling point over 90 °C). The main part of ethanol (~97% v/v) is found to form azeotropes- the reason for the fuel's high volatility.

Cooper et al. [7] presented a comparison of NIR, mid-infrared (MIR, 2.5-50 μm) and Raman spectroscopy for the determination of individual components such as benzene, toluene, ethylbenzene, ortho-xylene, meta-xylene and para-xylene in blended commercial gasolines. They concluded that Raman and MIR data yields lower standard errors as compared to NIR, whereas MIR has slightly lower standard errors than Raman. The simultaneous measurement of important components such as xylene isomers and other hydrocarbons in p-xylene production process were

* Corresponding author : saj@pinstech.org.pk

studied by Chung et al. [8-10] by preparing mixtures of these components and collecting their NIR spectra in the range 1100 to 2500 nm. They also compared NIR and MIR spectroscopic techniques for the determination of distillation temperatures of kerosene and NIR was found to have better calibration performance over MIR. They utilized NIR spectroscopy for monitoring the pour point of the lube base oil (LBO) in an on-line manner and concluded that it provides much faster measurement with similar precision as compared with the conventional on-line pour-point analyzer.

Pasquini et al. [11,12] coupled a fast-scanning acousto-optic tunable filter-based NIR spectrometer to the distillation apparatus for monitoring the condensed vapor in real time. The usefulness of the real-time monitoring of distillation is demonstrated using some standard binary mixtures and by comparing the distillation behavior of the adulterated and regular gasoline samples by obtaining their absorbance spectra.

To achieve the quality assurance efficiently, in every aspect of life, innovative and fast techniques are always being explored. In this energy deficient era, new approaches are being adopted to save the consumption of fuel especially petrol. A blend of ethanol and petrol in various proportions is a strong candidate fuel and some countries (especially Brazil) are already using this mixture in their vehicles. Pakistan is also taking step forward and E10 i.e. 10 % ethanol in petrol is being sold on experimental basis. The aim of the present study is to look for the ways to assure the quality of the ethanol and petrol mixture. For this purpose, NIR spectroscopy is chosen because it is a fast, cheap and reliable method to check the adulteration. The method of NIR absorption spectroscopy reported here is not novel but vision approach is simple and useful for the quality assurance.

2. Experimental

The experimental setup for NIR absorption spectroscopy of the selected pairs of liquid organic compounds is shown in Fig. 1. All the pairs contained in a quartz cuvette of size 10x10 mm were irradiated by a light source LS-1 (Tungsten-Halogen) and detected by NIR-512 spectrometer of Ocean Optics, UK in the wavelength range from 850 to 1700 nm to get absorption spectra. The spectrometer has a CCD detector and is connected to the computer via USB port to transfer the data.

The various combinations such as ethanol/commercial petrol; benzene/ethanol; toluene/commercial petrol and toluene/benzene were selected. The reference and dark spectra were recorded. The built-in software automatically subtracts the effects of the reference and dark spectra and provides the absorption results. First of all absorption spectra of 100% pure solvents are taken. Then in a given pair e.g. ethanol/petrol, percentage of ethanol is varied in steps of 5% up to maximum 50% and for each step absorption spectrum is recorded. For 5% ethanol the balance 95% is petrol. Similarly the same procedure is followed for other pairs. The absorption spectra are plotted and analyzed. The chemicals used in the experiments were of extra pure (>99%) made by different companies; ethanol by Labscan, Poland; benzene by Merck, Germany, toluene by AnalaR, UK; petrol by Shell pump.

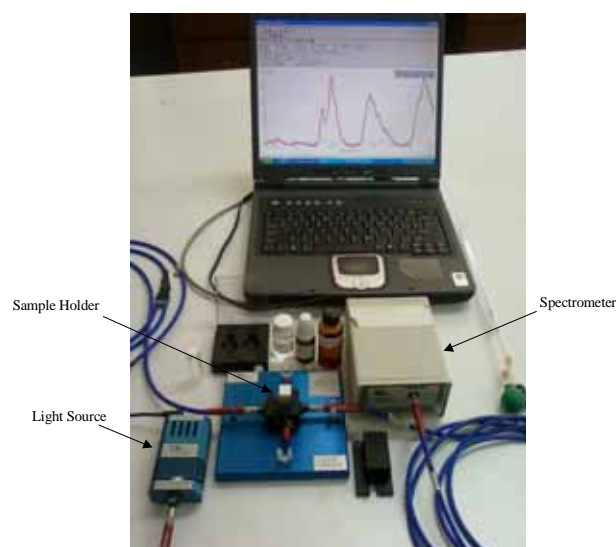


Figure 1. Experimental setup for near infrared (NIR) absorption spectroscopy.

3. Results and Discussion

Figures 2-5 show the NIR absorption spectra of four pairs of organic liquid compounds in the various proportions at an integration time of 100 milli-sec along with the calibration curves drawn out of the spectra. Figures 2, 3, 4 and 5 display the results for ethanol in petrol, benzene in ethanol, toluene in petrol and toluene in benzene, respectively. All the spectra contain distinctly separable wavelength ranges where the variation in the intensity corresponding to the concentration is prominent. Fig. 2a gives 1400-1650 nm wavelength range where the absorption intensity for 100%

ethanol is the maximum whilst for 100% petrol it is the minimum. In Fig. 3a for 1125-1150 nm wavelength range, the absorption intensity at the top is for 100% benzene whereas at the bottom it is for 100% ethanol. Similarly, Fig. 4a exhibits 1130-1150 nm wavelength range in which the absorption intensity for 100% toluene is the highest and for 100% petrol it is the lowest and in Fig. 5a, from 1175 to 1210 nm spectral range, the absorption intensity value is the maximum for 100% toluene whereas its minimum value shows the results for 100% benzene.

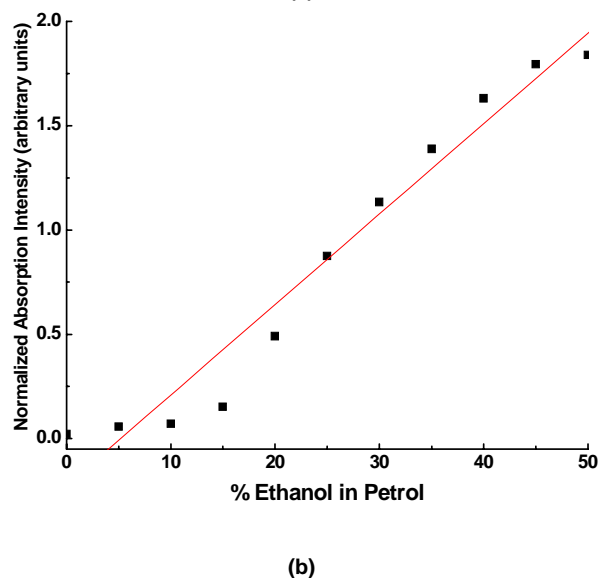
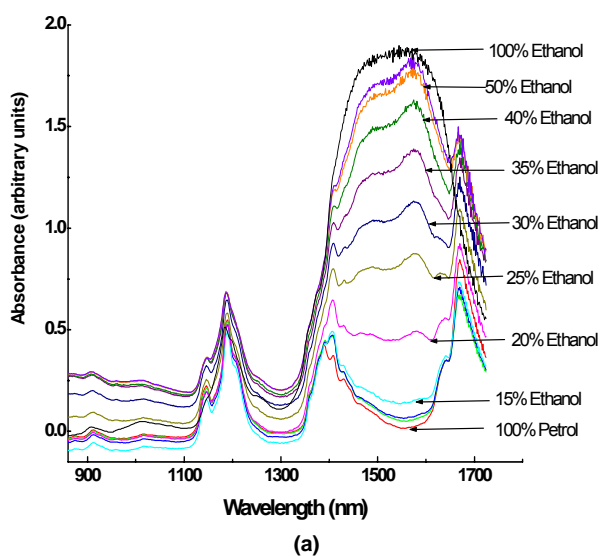


Figure 2. (a) NIR absorption spectra of various proportions of ethanol in commercial petrol (b) Calibration curve for ethanol in petrol at 1575 nm.

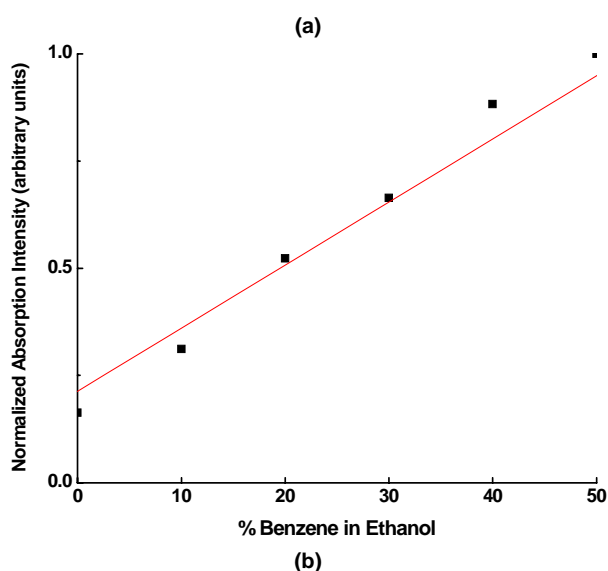
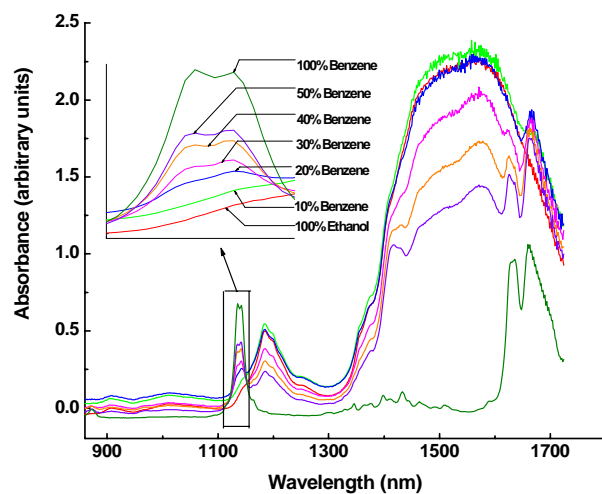


Figure 3. (a) NIR absorption spectra of different compositions of benzene in ethanol (b) Calibration curve for benzene in ethanol at 1135 nm.

The calibration curves are shown in Fig. 2b, 3b, 4b and 5b. These curves are plotted by varying the proportions of the pair of organic solutions upto 50% along x-axis whilst absorption peak intensity, in arbitrary units (a.u), of an optimal wavelength selected from a distinct spectral range is drawn along y-axis. The linear fitting is performed on the data points and Table 1 summarizes the results of linear fit for four organic pairs. The table clearly indicates that all the pairs have unique slopes and regression values close to one. These graphs can be used in quality control applications to determine the proportions of any one component from the pair of solutions. Fig. 2b plots the absorption intensity taken from Fig. 2a at 1575 nm for different percent-

Table1. Linear fitting parameters of calibration graphs for pairs of organic solvents.

Organic pair	A (y-intercept)	B (slope)	R (linear regression)	SD (standard deviation)
Ethanol/petrol	-0.22395	43.33×10^{-3}	0.97898	0.15779
Benzene/ethanol	0.08876	6.14×10^{-3}	0.99382	0.02486
Toluene/ petrol	0.54441	7.73×10^{-3}	0.9683	0.03484
Toluene/benzene	0.00824	2.81×10^{-3}	0.98625	0.00755

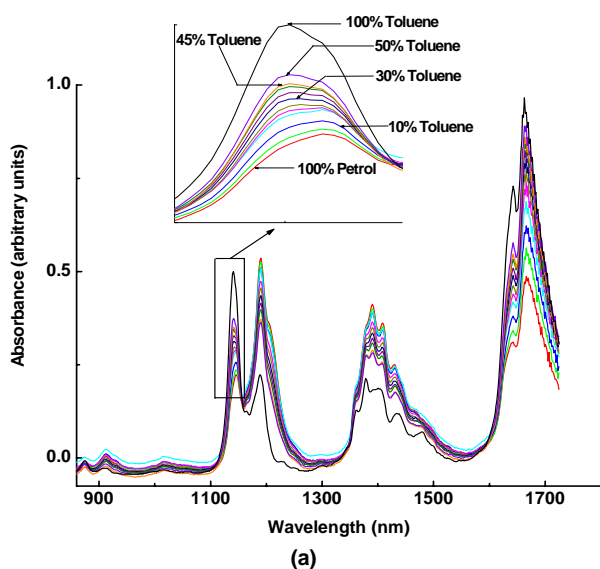


Figure 4. (a) NIR absorption spectra of different percentages of toluene in petrol (b) Calibration curve for toluene in petrol at 1139 nm.

ages of ethanol in petrol. In Fig. 3b, results from Fig. 3a at 1135 nm are displayed for various proportions of benzene in ethanol. Fig. 4b shows the results extracted from Fig. 4a for various compositions of toluene in petrol at 1139 nm and in

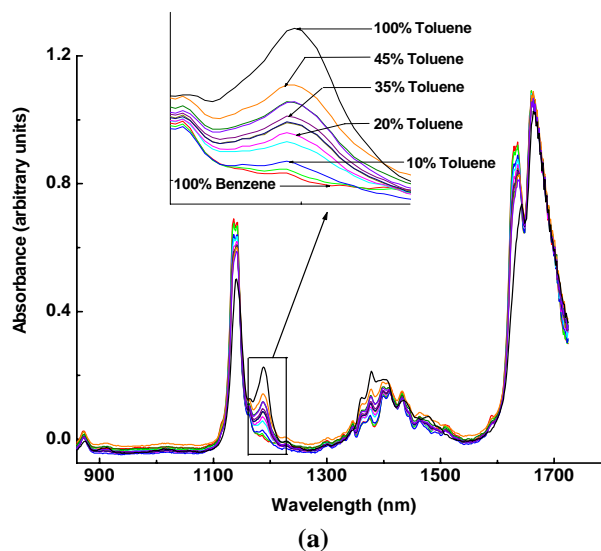


Figure 5. (a) NIR absorption spectra of various compositions of toluene in benzene (b) Calibration curve for toluene in benzene at 1187 nm.

Fig. 5b the results extracted from Fig. 5a at 1187 nm are plotted for various percentages of toluene in benzene. The observed trend in all the above-mentioned four calibration plots is almost linear with respect to varying percentage concentration.

For overlapping wavelength ranges such as benzene/ethanol and toluene/petrol pairs it is still possible to draw calibration curves because the slopes of the straight lines are different. But for more reliable results, a complete absorption spectrum might be considered before taking data at selected optimum wavelength. Since both pairs exhibit characteristic shape of spectrum therefore one can avoid the mixing of pairs.

4. Conclusions

NIR absorption spectroscopy of ethanol/commercial petrol; benzene/ethanol; toluene/commercial petrol and toluene/benzene pairs is performed for various combinations and ratios. In the wavelength range 850–1700 nm, all the organic pairs exhibit narrow band of distinguishable spectral ranges where the effect of concentration change is clearly separable. The shape of the absorption spectrum is unique for each set of the organic chemicals and may help recognize the pair. The pair concentration at selected wavelength in the characteristic spectral range was used to draw the calibration curves, which may be employed for the quality control application, since the linear fit results in straight line with a specific slope for each set of the organic solvents.

Acknowledgements

PINSTECH provided financial assistance for this work from its R & D grant. We are grateful to Dr. Akbar Ali, Chemistry Division for providing us the organic solvents.

References

- [1] J. Workman and J. L. Weyer, Practical Guide to Interpretive Near Infrared Spectroscopy, CRC Press, USA, 2008.
- [2] Y. Lee, H. Chung and N. Kim, Appl. Spect. **60** (2006) 892.
- [3] R. M. Balabin, R. Z. Safieva and E. I. Lomakina, Chemo. and Intell. Lab. Sys. **88** (2007) 183.
- [4] R. M. Balabin, R. Z. Syunyaev and S. A. Karpov, Energy & Fuels **21** (2007) 2460.
- [5] R. M. Balabin and R. Z. Safieva, Fuel **87** (2008) 1096.
- [6] R. M. Balabin, R. Z. Safieva and E. I. Lomakina, Analytica Chimica Acta **671** (2010) 27.
- [7] J. B. Cooper, K. L. Wise, W. T. Welch, M. B. Sumner, B. K. Wilt and R. R. Bledsoe, Appl. Spect. **51** (1997) 1613.
- [8] H. Chung, J. -S. Lee and M. -S. Ku, Appl. Spect. **52** (1998) 885.
- [9] H. Chung, M. -S. Ku and J.-S. Lee, Vibr. Spect. **20** (1999) 155.
- [10] H. Chung and M.-S. Ku, Appl. Spect. **57** (2003) 545.
- [11] C. Pasquini and S. H. F. Scafi, Anal. Chem. **75** (2003) 2270.
- [12] C. Pasquini and A. F. Bueno, Fuel **86** (2007) 1927.

