Application of FTIR Spectroscopy Coupled with Attenuated Total Reflectance for the Determination of Trimethyl Borate

M. B. Pişkin, M. Sarı Yılmaz

***Abstract*—** Trimethyl borate (TMB), a very important organo-boron compound, has a wide range of industrial applications. Moreover TMB is used in the production of $NaBH_4$, is a hydrogen carrier and storage media, as a starting material.

The determination of the TMB concentration in the TMB-methanol (TMB-M) azeotropic mixture is hard by the conventional analyses methods. In the present study, it was aimed that to develop a technique for the fast and accurate determination of unknown concentration of the TMB in the TMB-M azeotropic mixture. The FT-IR absorbance peak height showed a linear dependence on the TMB concentration in the wavenumber range 1250 to 1425 cm^{-1} for samples with TMB concentrations 5 to 100 wt% in methanol. Correlation coefficients, R^2 of 0.9994 were obtained using the regression analysis. In addition, during the production of TMB, the samples were withdrawn randomly from the obtained azeotrope solution in order to determine the unknown concentration of TMB by FTIR spectroscopy. The results indicated that this method has been applied successfully to quantify TMB in TMB-M azeotrope.

***Keywords*—** ATR-FTIR, Hydrogen Storage, $NaBH_4$, Trimethyl Borate, Quantitative Analysis.

I. Introduction

THE organo-boron compounds are very important materials for chemical and metallurgy industries. One of these organo-boron compounds, having commercial importance, is trimethyl borate (TMB). TMB is used as a solvent or catalyst for the production of resins, waxes, paints and varnishes, as a methylation agent or as a boron source in organic reaction to manufacture biocides, flame retardants for textile and in welding fluxes, anti-oxidants, corrosion inhibitors, tackifiers for elastomers and rubbers, cross-linking agents for polymer, dehydrating agents, and plastic stabilizers [1].

Recently, the use of methyl borate in the energy field and the importance of commercial boron compounds class are growing gradually. When the production technologies of sodium borohydride ($NaBH_4$) are investigated it is seen that there are methods in which TMB is used as a starting material [2], [3]. $NaBH_4$ has a great hydrogen storage capability, it is more stable compared to other chemical hydrides and converts to hydrogen, key energy solution for the 21st century, more easily in presence of catalysis [4], [5].

The production of methyl borate esters have been investigated for many years. The determination of TMB concentration in the azeotrope mixture is a significant knowledge for production process of $NaBH_4$ which is excellent hydrogen storage medium. Although there have been too many investigations of production of methyl borate esters, there is only one study on the determination of TMB concentration in the literature. Kaye and Sordyl developed the method for determining the composition of methanol - trimethyl borate mixtures. They prepared the several mixtures of pure methanol and trimethyl borate compounds and determined the densities and refractive indices of these mixture for analysis of' the curves. The results showed that greater accuracy in determining the composition was possible from a density determination [6].

The determination of the TMB concentration in the TMB-methanol (TMB/M) azeotropic mixture is hard by the conventional analyses methods. For this reason, the present study employed the quantitative FTIR analysis as it can be performed without the separation of the mixture into the individual components**.**

Quantitative measurements for the liquid and solid samples are quite common by using Fourier transform infrared spectroscopy (FTIR) spectroscopy [7]-[12]. The uses of infrared as a quantitative tool have increased significantly. Therefore, applying this vibrational technique offers several advantages in comparison to the other analytical methods, such as rapid and easy sample preparation, short analysis time and the use of a minimal amount of sample [13]. Quantitative analysis in IR spectroscopy is governed by Beer's Law [14], the simplest situation is a single-component analysis where it is necessary to identify an absorbance band which can be measured and calibrated by reproducible procedures [15].

To the best knowledge of the authors, no attempts have been made in using FTIR for quantitative analysis of TMB formed in the binary mixture. This paper aims to describe a simple method that can be used for on-line measurements of the TMB concentration in TMB-M azeotrope.

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II. EXPERIMENTAL PROCEDURE

A. Materials and Methods

Borax used in this investigation was obtained from Eti Mine Works, Turkey. TMB ($B(OCH_3)_3$) and M (CH_3OH) purchased from Merck were used as reference materials to investigate the characteristic properties of TMB and M and prepare the calibration curve.

Infrared spectra were recorded using a Perkin Elmer Spectrum One spectrometer equipped with a universal diamond attenuated total reflectance (ATR) top-plate. The resolution of the collected spectra was set to 4 cm^{-1} and co-addition of four scans per spectrum was applied in the 4000 to 650 cm^{-1} range.

B. Synthesis of TMB

As previously reported, TMB is synthesized by an esterification reaction (1) of borate with methanol in concentrated sulfuric acid [16]. The overall reaction is as follows:

$$Na_2B_4O_7.10H_2O+2H_2SO_4+16CH_3OH\rightarrow 4(B(OCH_3)_3CH_3OH))+2NaHSO_4+17H_2O \quad (1)$$

The reaction mixture was introduced into a glass reactor according to stoichiometric ratios of (1) and heated to adjusted temperature based on the boiling points of azeotrope. Then, the mixture was fractionally distilled and as a result of heating the TMB-M azeotrope solution was obtained.

During the production process, the samples were withdrawn randomly from the obtained azeotrope solution in order to determine the concentration of the TMB by FTIR spectroscopy.

C. Preparation of a Calibration Curve

The FTIR spectra of TMB and M displays three joint absorption peaks: 2952-2831 cm^{-1} (C-H stretching bands), 1480-1448 cm^{-1} (C-H stretching bands), and 1179-1020 cm^{-1} (C-O stretching bands), as shown in Fig. 1. The other absorption band at 3315 cm^{-1} in the infrared spectrum of M is assigned to (O–H) stretching vibrations. The absorption band at 1331 cm^{-1} in the infrared spectrum of TMB corresponds to characteristic B-O stretching [16]. This peak was chosen as an individual peak for the quantitative determination of TMB in the TMB-M azeotrope.

The various concentrations of the TMB solutions (5, 10, 20, 30, 40, 50, 60, 80, and 100 wt%) were prepared for the calibration curve. The FTIR spectrums of the calibration solutions are shown in Fig.2.

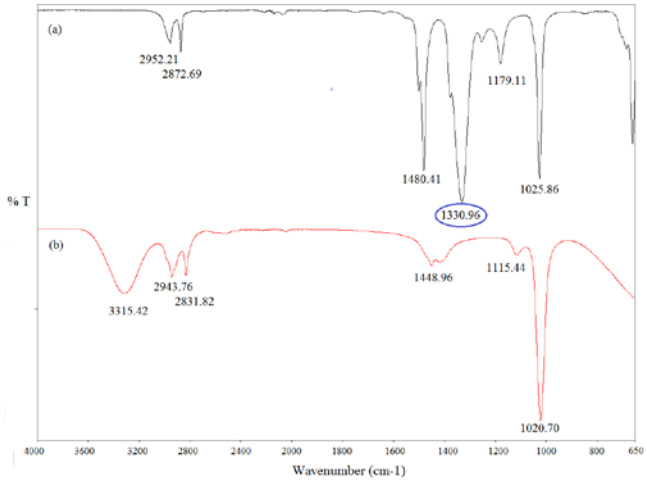

Fig.1 FTIR spectrums of two reference materials a) TMB and b)M

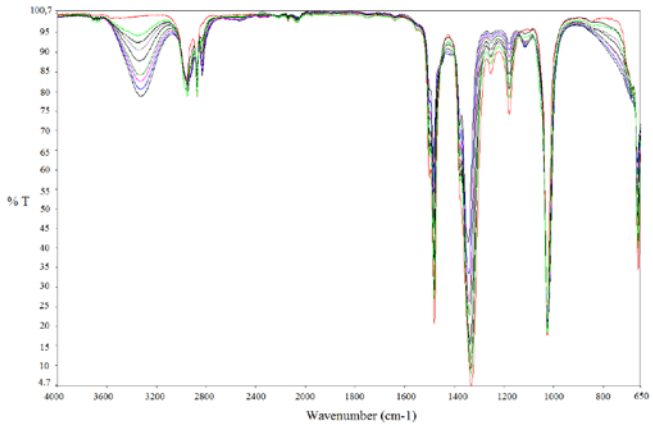

Fig.2 FTIR spectrums of the various concentrations of the TMB

III. RESULTS AND DISCUSSION

Calibration line was constructed by plotting the measured height against the concentration of known amounts of the TMB (%) in the TMB-M azeotrope mixture to obtain best straight line with maximum correlation coefficient (0.9994) (Fig.3). The high degree of linearity in the calibration curve relies on the absorbance of the analytical band obeying the Lambert-Beer Law.

Data analysis was carried out according to a linear algorithm was expressed to determine of the TMB concentration. The calibration line is in the form of a linear equation is given below:

$$Y = mX + n \quad (2)$$

Y = Concentration of TMB (%)
X = Calculated height of band region of B-O
m = slope = 68.67
n = intercept = 1.63

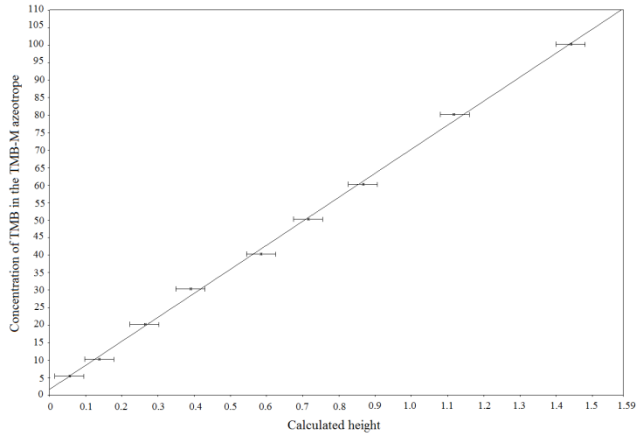

Fig.3 Calibration curve according to the Beer-Lambert law for the quantitative determination of TMB in the azeotrope. The Perkin-Elmer software has automatically plotted the concentration (%) vs. the calculated height of the characteristic B-O peak.

The accuracy of the calibration curve was investigated through the preparation of a solution containing 55% (wt) TMB that was analyzed through IR spectroscopy. The relative error between the absorbance of the theoretical value (from calibration curve) and the experimental value was found as 1.90%.

In order to determine the concentration of the TMB in the obtained TMB-M azeotrope, the samples were withdrawn randomly during the production process. The variations of the characteristic B-O band in the FTIR spectra are shown in Fig. 4.

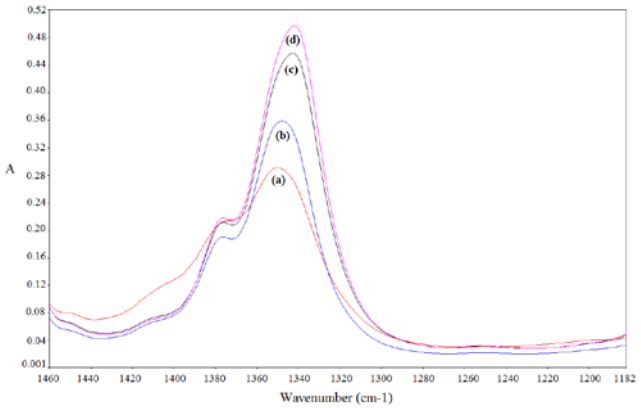

Fig. 4 Overlaid FTIR spectra of the characteristic B-O band in the obtained azeotrope solution at different times a) 5 min, b) 30 min, c) 60 min, and d) 90 min

The variations in the concentration of TMB, calculated from the calibration curve, as a function of time is given in Fig. 5. It was observed that the concentration of the TMB increased in time.

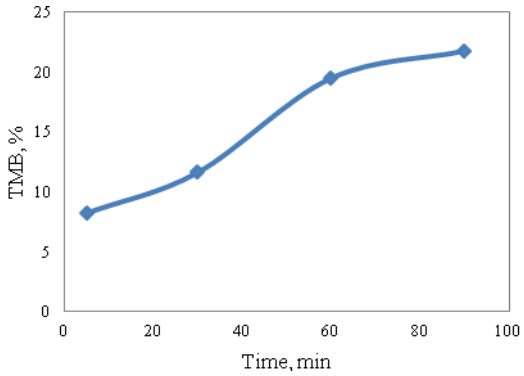

Fig. 5 Variations in the TMB concentration in the obtained TMB-M azeotrope as a function of time

IV. Conclusion

In this study, attenuated total reflection Fourier transformed infrared spectroscopy (ATR–FTIR) technique can be successfully performed for the quantitative determination of TMB in TMB-M azeotrope for the first time.

The present study has provided a very useful method for determining the concentrations of TMB, which is fast, simple, and reliable.

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