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A Rapid and Reproducible Near Infrared Spectroscopy based Method for Solvency Power Measurement of Dearomatized Solvents

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ABSTRACT

Today, dearomatized hydrocarbon solvents are widely used in manufacturing, cosmetic, and fast moving consumer goods sectors due to onset of stringent environmental norms. Conventionally, the solvency of such solvents is measured in terms of Kauri Butanol (KB) value. The measurement of KB value, as per ASTM-D1133, is costly, time consuming, and tedious process. To overcome such limitations, the present study reports, an innovative method using Fourier Transform-Near Infra-Red (FT-NIR) spectroscopy based rapid and reliable technique for estimation of solvency power. Partial least squares regression was used to develop calibration and prediction of KB value by the use of TQ Analyst 8 software associated with FT-NIR analyzer. This method is fast, safe, reliable, nondestructive, and inexpensive contrary to conventional procedures. The results obtained based on developed method are found to be in good agreement with those reported based on standard test method, that is, ASTM-D1133.

Key words: Kauri Butanol value, Solvency power, Fourier transform-near infra-red spectroscopy.

1. INTRODUCTION

Growing environmental concerns worldwide has added impetus to adopt environmentally benign solvents in production processes. As a result of this, use of dearomatized solvents is increasing across manufacturing of fast moving consumer goods, paints, foodstuffs, packaging, electronic, tyres, etc. Dearomatized Solvents Market to grow from USD 1561 million in 2016 to USD 2198 million by 2022, at a compound annual growth rate of 5.9% during the forecast period. Growth in the automotive and construction industries is expected to drive the demand for petrochemical-based solvents during the forecast period [1].

Typically, dearomatized solvents are produce by hydrogenation of petroleum fractions, with boiling range of 60–330°C, [2,3] thereby converting aromatic content of those fractions to naphthenic and paraffinic. Although, such transformation brings down solvency of treated petroleum fractions but imparts eco-friendly nature to end product. Today, dearomatized solvents derived from kerosene and light diesel fraction finds applications in numerous industries and is classified in terms of their flash points. The composition of such solvents predominately contains n-paraffin, iso-paraffin, and naphthenic species. The presence of aromatic and naphthenic species imparts solvency power to solvents and is traditionally measured in terms of Kauri Butanol (KB) value. The KB value shows that solvent is more aggressive/active in the ability to dissolve certain materials. It is being measured by ASTM D1133 method [4].

Some of other chromatographic methods were also used to predict solvency power of hydrocarbon solvents for evaluating the solvency characteristics of petroleum hydrocarbons that are used as solvents and thinners in organic coatings. The method makes use of the principles and practices of thin-layer chromatography [5].

However, ASTM D1133 is universally accepted and widely used to predict KB value of hydrocarbon solvent. Even some of publications also found on the use of biodiesel as a good solvent properties, a feature rendered additionally attractive by its biodegradability, low toxicity, and low content of volatile organic compounds. The KB value is a parameter used for describing, the KB values of individual fatty acid alkyl esters were determined. The KB values of fatty esters depend on chain length, including the alcohol moiety, and unsaturation, a phenomenon observed similarly in hydrocarbons [6].

The ASTM D1133 method is titration method and time consuming. Furthermore, the solvent KB resin is costly, has limited shelf life and requires dry storage conditions for storage purpose at constant 25°C. A number of literature is available on Near Infra-Red (NIR) multivariate calibration models to predict physical properties of aromatic-rich hydrocarbon mixtures [7]. However, literature on solvency power, that is, determination of KB value is not available. These limitations bring out to need of an alternative novel method for quick and economical measurement of KB value. This makes the present study meaningful and novel.

In the present study, a quick and reliable method by the use of Fourier Transform NIR (FT-NIR) spectroscopy associated with TQ Analyst 8 software using Partial Least Square (PLS) calibration model is envisaged [8-10]. The use of spectroscopic methods NIR is a rapid, accurate and precise as compared to ASTM method. Therefore, the present study deals with development of rapid and accurate FT-NIR based methodology for fast estimation of KB value of hydrocarbon/Dearomatized solvents. The developed method can be used as a quick screening tool for determination of

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KB value of hydrocarbon solvents with minimum sample quantity for R and D purpose.

2. EXPERIMENTAL PROCEDURE

2.1. Samples

The selection of samples for calibration is critical, because informative samples could provide adequate variance for analysis. For this purpose to cover lowest to highest range of KB value, blends of Heptane, Toluene and Paraffin liquid at room temperature (preferably 25°C) on volume basis were prepared (Table 1). HPLC grade Toluene and Heptane (>99%) and IR grade liquid paraffinic oil from Merck were used for the preparation of calibration samples. The KB value of toluene, heptane, and paraffin liquid is 105, 25, and 12 (approximately) by standard ASTM D1133 method and the variance in their KB value is the reason of selection them as calibration samples. In general, the KB values of De aromatized solvents falls between 25 and 31; hence, most of the calibration samples were prepared in this range.

2.2. KB Value

The KB value of each of the blend (calibration samples) was determined by standard ASTM method D1133. The determination of KB value of hydrocarbon solvents used in paint and lacquer formulations is measured by ASTM D1133 method [4]. It is a titration method and KB value is defined as “The volume in milliliters at 25°C of the solvent, corrected to a defined standard, required to produce a defined degree of turbidity when added to 20 g of a standard solution of kauri resin in normal butyl alcohol.”

In brief, 20 g of the KB solution taken into a 250 mL Erlenmeyer flask. Check that the temperature of the KB solution in the flask is 25°C. If not, place the Erlenmeyer flask and its content in a water bath maintained at 25°C and allow to equilibrate for at least 30 min. Remove the flask from the water bath. Fill the 50 mL burette with the solvent being tested and titrate the solvent into the Erlenmeyer flask with constant swirling. Gradually reduce the successive amounts of solvent added as the end point is approached. The end point is reached when the sharp outlines of 10-point print placed directly beneath the water bath and observed through the liquid are obscured or blurred, but not to the point where the print becomes illegible. Check the temperature in the flask immediately after the end point has been reached and if over 30°C or under 20°C, repeat the titration. Designate the volume of solvent, in milliliters, to produce turbidity.

Table 1: KB values of blends of heptane, toluene, and paraffinic liquid (v/v%).

S. No.	Heptane	Toluene	Paraffin liquid	KB value (ASTM D1133)
1.	50	0	50	18.2
2.	70	0	30	20.7
3.	80	0	20	22.0
4.	100	0	0	24.7
5.	95	5	0	26.7
6.	90	10	0	29.8
7.	89	11	0	31.6
8.	85	15	0	32.8
9.	80	20	0	35.2
10.	75	25	0	39.0
11.	60	40	0	48.8
12.	50	50	0	57.8
13.	30	70	0	76.7
14.	20	80	0	86.6
15.	10	90	0	95.2
16.	5	95	0	100.5
17.	0	100	0	104.8

KB: Kauri Butanol

All the samples were performed in duplicate and average value was used for calculation.

Samples with adequate variances could generate a robust model. The samples of same sets of blends are used for recording NIR spectrum.

2.3. Recording of FT-NIR Spectra

The Thermo Scientific Antaris II FT-NIR analyzer, with FT technology is used for scan of calibration samples. The Antaris II spectrometer is optimized for the use in the NIR spectral region (10,000–4,000 cm^{-1}) or (1000–2,500 nm). The resolution used for scan is 4 cm^{-1} and the number of scan per sample is 32. The samples were placed on Antaris liquid analyzer in tubes (2 × 60 mm) placed in sample cell. All the spectrum were collected using replicate samples.

2.4. Chemometric Software

The measured spectra of calibration samples were analyzed using quantification software TQ analyst 8 to develop calibration model to predict KB value using PLS regression model. For this purpose, automatic region selection tool in TQ analyst 8 software, identified three region of spectrum range, namely, 6286–6071 cm^{-1}, 7388–6387cm^{-1}, and 8782–8620 cm^{-1} (Figure 1a-c) has been exploited for quantification that has been automatically selected by chemometric software TQ Analyst 8. Using software TQ analyst 8, PLS algorithm examined all the above three specified regions of the calibration spectra to determine which areas are varying statistically as a function of component concentration.

The PLS calibration model is developed in one operation using spectral and actual KB values (ASTM D1133) information from the calibration samples by software (Figure 2).

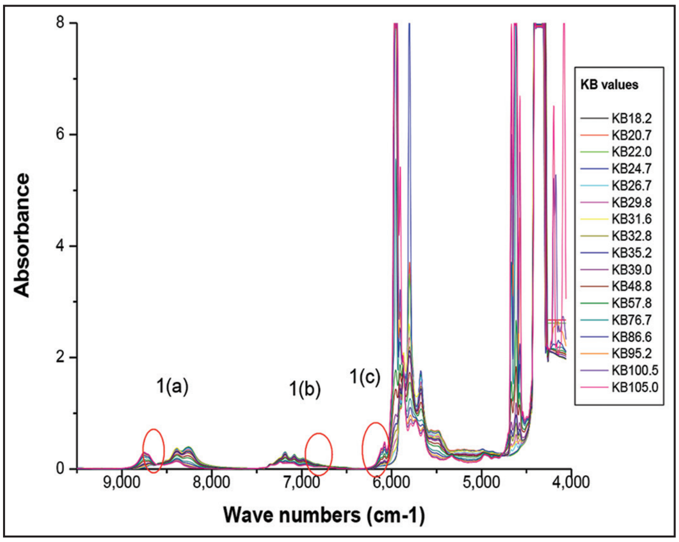

Figure 1: Near infrared overlaid absorbance spectra (Full range) of all the calibration samples representing different Kauri Butanol values. Labels 1a-c is the spectral region as selected by software TQ Analyst 8 for PLS regression model.

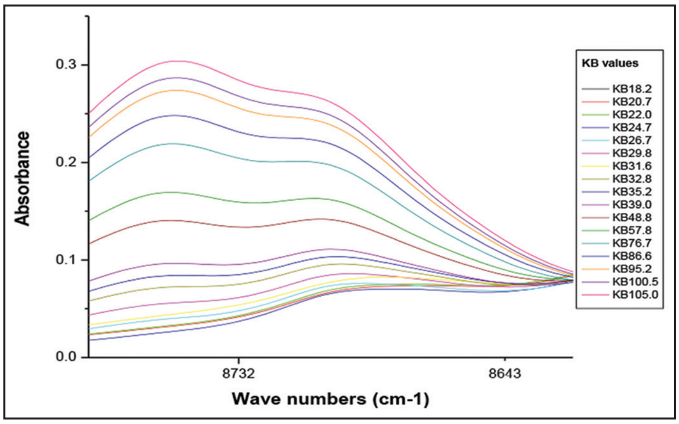

Figure 1a: Near infrared overlaid absorbance spectra (8782–8620 cm^{-1}) of calibration samples representing different Kauri Butanol values.

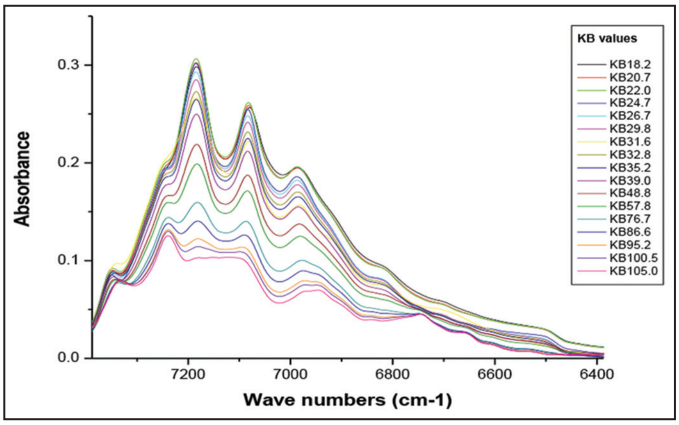

Figure 1b: Near infrared overlaid absorbance spectra (7388–6387 cm^{-1}) of calibration samples representing different Kauri Butanol values.

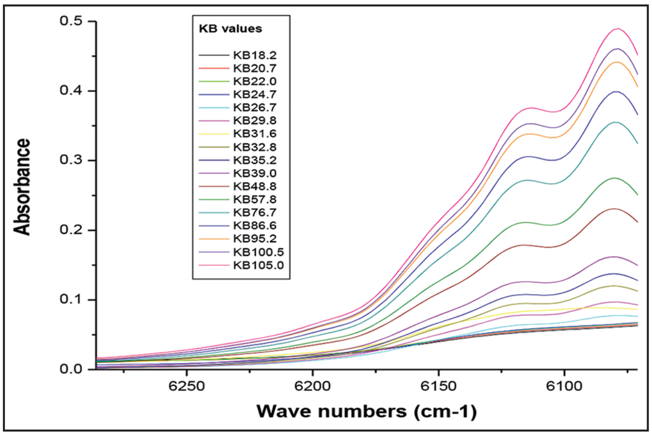

Figure 1c: Near infrared overlaid absorbance spectra (6286–6071 cm^{-1}) of calibration samples representing different Kauri Butanol values.

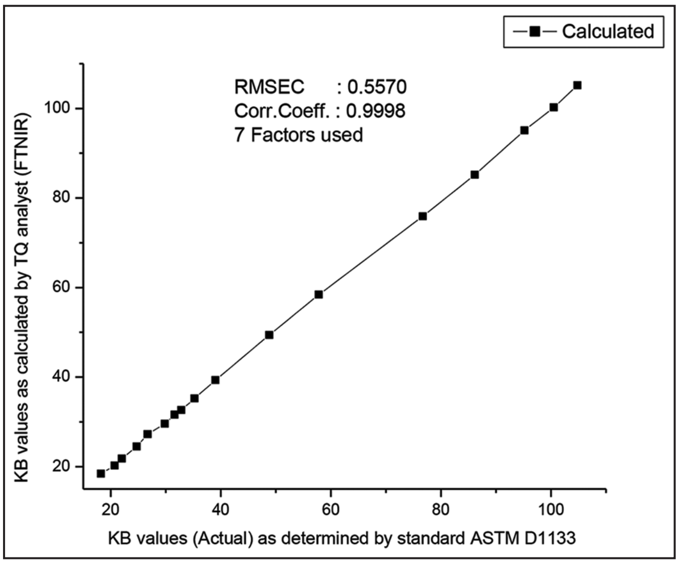

Figure 2: Prediction model between actual versus calculated values by TQ Analyst 8 Software using partial least square regression model.

3. RESULTS AND DISCUSSION

The results obtained from FT-NIR spectrometer are compared with the standard method of determination of KB value as per ASTM D1133 procedure.

The KB values for different blends (Calibration samples) of varying ratio of Heptane, Toluene, and Paraffinic liquid were determined using ASTM D-1133 and results are given in Table 1.

The same set of calibration samples (as defined in Table 1) of equal volume were used to record FT NIR spectra to develop calibration model using PLS regression model associated with NIR spectrometer. Figure 1 shows the overlaid absorption spectra of the calibration samples having different KB values assigned in different colors. The overlay absorption spectra of all the Calibration samples in the spectral region (10,000–4,000 cm^{-1}) employed for calibration were presented (Figure 1). Although all spectra were recorded using the full range of spectrometer, automatic region selection tool in TQ analyst 8 software identified three region of spectrum range, namely, 8782–8620 cm^{-1}, 7388–6387cm^{-1}, and 6286–6071cm^{-1} Figure 1a-c, respectively, has been exploited for quantification. More pronounced spectral variance were found in above three regions and PLS regression model was developed by the use of variance of different calibration samples by software. Figure 1a-c depicts more clearly the variance in absorption and use of this spectrum range namely 8782–8620 cm^{-1}, 7388–6387 cm^{-1}, and 6286–6071 cm^{-1}, respectively, for the development of prediction model. Overlaid absorption spectra of each calibration samples having assigned KB value were represented in different color (Figure 1a-c).

NIR absorption bands arise from overtones and combinations of the fundamental mid-IR molecular vibrations often associated with hydrogen atoms [11-13].

In organic solvents, the absorption bands originate predominantly from combination or overtone absorption of the CH groups of their aliphatic and aromatic hydrocarbon parts [12]. A NIR spectrum of the CH groups usually shows the series of absorption group, which are unevenly distributed over the region from 4000 cm^{-1} to 10000 cm^{-1}, as shown in Figure 1.

The goal of the study is to development of calibration model using the difference in absorption pattern of solvents from aliphatic to aromatic. As we know that KB value of solvent increases from paraffinic to aromatic and they have different absorption pattern, for example, in the spectra of heptane and paraffinic liquid (Figure 3) a series of absorption groups present over the range of 4000–10000 cm^{-1}. The strongest absorption group in the 4000–4400 cm^{-1} region is assigned to the first-order combination bands of the CH2 and CH3 groups [14]. The

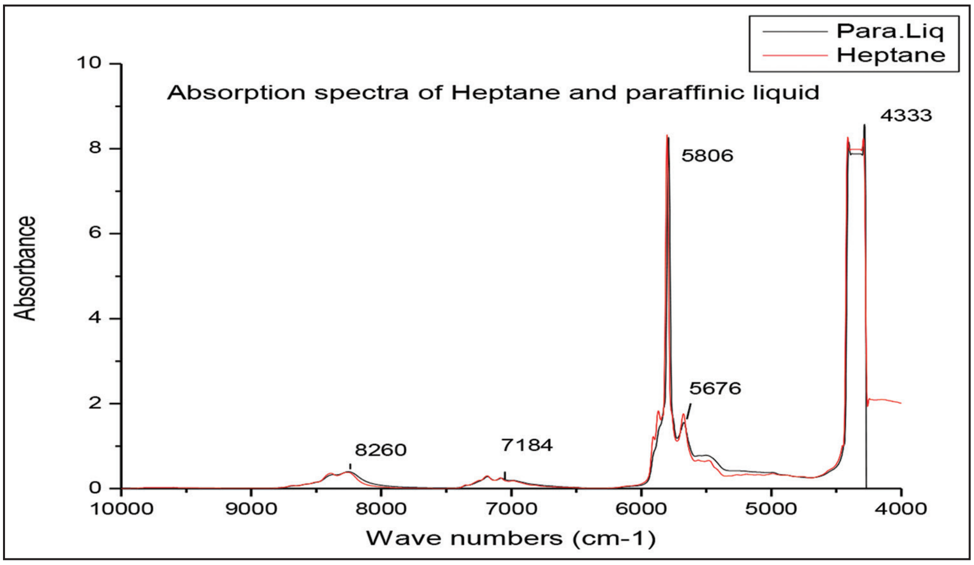

Figure 3: Near-infrared overlaid absorbance spectrum measured with a liquid cell of a Heptane and Paraffinic liquid (Aliphatic).

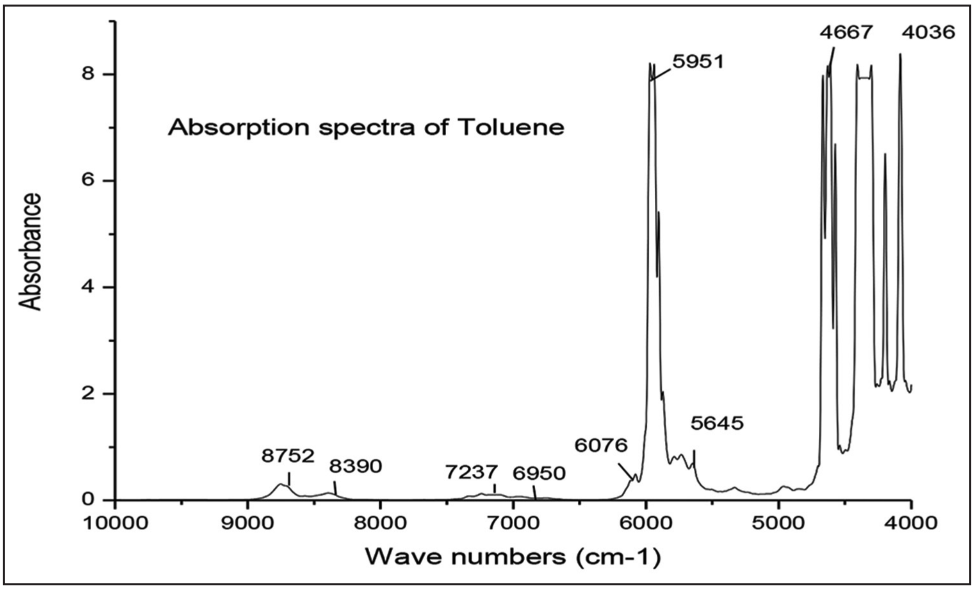

Figure 4: Near-infrared absorbance spectrum measured with a liquid cell of a Toluene (Aromatic).

absorptions in the 6000–5700 cm^{-1} region are assigned to the first-order overtone bands of the CH type. The above two groups represent the main NIR absorptions of CH groups in the 10000–4000 cm-1 region of aliphatic hydrocarbons. Weak absorptions in the 7200–6700 cm^{-1} and 8500–8000 cm^{-1} regions are assigned to the second-order combination of the deformation and stretching of CH group.

The absorption pattern is almost same for heptane and paraffinic liquid (Figure 3). On the other hand, the absorption pattern of aromatic is quite different from aliphatic compounds, Figure 4 shows the NIR spectrum of toluene. The spectrum has several absorption groups, each of which has a combination or overtone type as the spectrum of heptane but is notably different in the 4700–3500 cm^{-1} region, and this represents the structural difference between toluene and heptane. Each absorption group of toluene is assigned to a combination or overtone type, on the basis of the frequencies of the fundamental bands of benzene [15].

Absorption group in 6200–5600 cm^{-1} region is due to the overlapped absorptions of the first order overtone of the CH stretching of both benzene and methyl groups. Other absorption groups, which appear around the 5500–4800 cm^{-1} and 7300–6600 cm^{-1} regions, are assigned to the second-order combinations of the CH stretching and CH deformation, respectively. The absorption groups in the 9800–8500 cm^{-1} and 8500–8200 cm^{-1} regions are assigned to the second-order overtone of CH stretching of the benzene and methyl CH group, respectively. The above explanation clearly shows how the pattern of absorption in NIR region is different for aromatic and aliphatic compounds. This variance in absorption pattern between Aromatic and Aliphatic compounds is the basis of prediction model for the determination of KB values when statistically exploited for PLS regression model using TQ Analyst 8 software.

Once the spectra from the calibration standard samples had been collected, they were opened in the Thermo Scientific TQ Analyst 8 chemometric software for quantitative model development. In the TQ Analyst software, calibration curves can be built using a variety of quantitation models, from single variable methods to the most robust multivariate statistical analysis algorithms. In this case, PLS regression model is adopted. The developed calibration model by the use of TQ Analyst 8 software, exploited spectral variation of calibration samples for PLS regression and straightforward able to predict KB value of

Table 2: Comparison of KB value of samples by FT-NIR and ASTM D1133 method.

S. No.	Blended samples (V/V %)		KB value by FT-NIR	KB value by (ASTM D1133)
	Heptane	Toluene		
1.	50	50	57.5	57.6
2.	60	40	48.9	48.8
3.	90	10	29.7	29.8
4.	85	15	32.6	32.7
5.	30	70	76.6	76.8
6.	10	90	95.0	95.1
7.	75	25	40.0	39.8
8.	78	22	37.1	36.8
9.	65	35	45.0	44.8
10.	D80 Solvent-1		30.2	30.3
11.	D-80 Solvent-2		31.0	30.8
12.	D-80 Solvent-3		29.2	29.5

KB: Kauri Butanol, FT-NIR: Fourier transform-near infrared

unknown sample. Correlation plot between standards (KB values obtained from ASTMD1133) versus calculated values (KB values obtained from FTNIR analyzer) is in good agreement (Figure 2). The KB value of all the calibration samples was performed in duplicate and average value was used for calculation as per standard method ASTM-D1133. Correlation coefficient 0.999 and root mean square error of calibration (RMSEC) 0.557 were obtained (Figure 2).

Table 1 show the KB values for different blends of varying ratio of Heptane, toluene and paraffin liquid determined by standard method (ASTM D-1133).

Further to validate the prediction model as developed using TQ analyst 8 software, set of unknown samples prepared by blend of toluene and heptane (v/v %) as well as samples of D-80 solvents were used to determine KB values by the use of FT NIR prediction model. The external validation of the method was performed with the samples of the validation set, that is, samples that are independent from those used to calibrate the method (Table 2).

D80, a widely used solvent, it is dearomatized aliphatic hydrocarbon which is transparent in appearance. It has very high flash point and manufactured by the de aromatization of Kerosene streams by solvent extraction. Three numbers of D80 samples of different batches were also used to predict KB values by developed PLS regression model using TQ Analyst 8 software along with other samples (Table 2).

Table 2 shows the KB values for samples as predicted by FT analyzer and determined by standard method (ASTM D-1133).

It is evident from Table 2 and Figure 5 that the results obtained from developed prediction model are comparable with the ASTM D-1133.

4. CONCLUSION

In the present paper an alternate and rapid method based on NIR spectral correlation approach, for the determination of solvency power, that is, KB value measurement has been developed. The developed method is useful to predict quick and cost-effective determination of KB value.

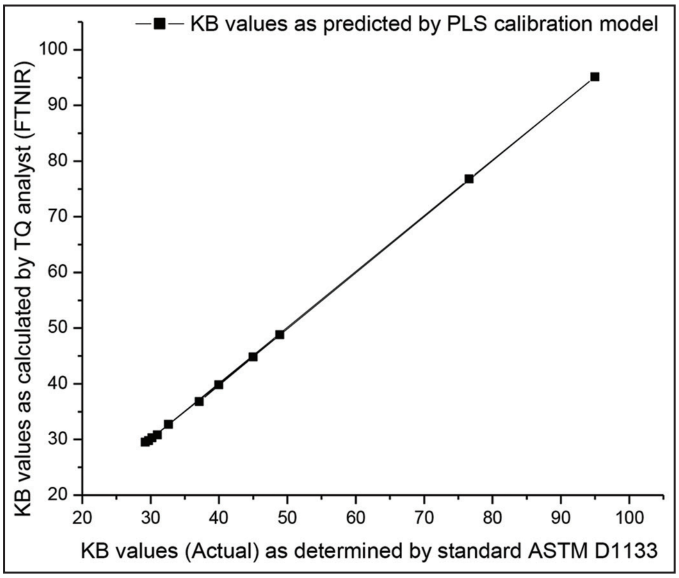

Figure 5: Graphical representation of Kauri Butanol values as Predicted by model using TQ Analyst 8 Software against actual values by standard method ASTM D1133.

The results so obtained are found to be in good agreement with those obtained over conventional ASTM D-1133.method. Correlation coefficient 0.999 and RMSEC 0.557 were obtained.

NIR can be used as alternative reliable method for determining KB value of commonly used solvents as well as dearomatized solvents.

The developed method is novel method and none of the literature available on the alternate method for the determination of KB value other than standard ASTM method. The way forward to use this technical advantage to the development of analytical applications of NIR as online quality monitoring tool for hydrocarbon solvents in manufacturing plants may be envisaged.

5. ACKNOWLEDGMENT

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*Bibliographical Sketch

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