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Estimation of Total Aromatics in Kerosene Fractions by Infrared Spectroscopy—II

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ABSTRACT

A general equation for the quick and accurate estimation of total aromatics in straight run kerosene fractions is derived using i.r. absorbances at characteristic wavenumbers from aromatic concentrates of kerosene of different crude oils. The accuracy of the method is found to be ±5%. *When compared with the FIA method the deviation was found to be within* 5·5%.

Key words: Infrared spectroscopy, kerosene fraction, total aromatics, regression analysis.

1 INTRODUCTION

The hydrocarbon-type compositions of petroleum fractions are key parameters for deciding their industrial utilities. The kerosene fraction is the primary source for production of ATF, naphthalenes and their precursors for dyes and intermediate industries and feed stocks for alkyl-benzenes for biodegradable detergents. The process development work for dearomatizing kerosene fractions by solvent extraction to produce ATF requires a fast and accurate method for estimation of total aromatics in the feed and its various fractions, and hence, would be of value in quality control of kerosene and turbine fuels.

Although the fluorescent indicator adsorption (FIA)[1] method is being used as the official method in the petroleum industry for estimation of paraffinic, olefinic and aromatic contents in gasoline and kerosene fractions, its shortcomings have by now been well recognized.[2,3] Recently Hayes and Anderson[4] have reported an HPCL method using dielectric constant detector for rapid determination of saturates, olefins and aromatics in petroleum distillates boiling up to 400°C. Riazi and Daubert[5] have developed correlations for prediction of hydrocarbon-type

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composition of petroleum fractions using readily available physico-chemical parameters. In a recent publication, Ramaswamy *et al.*[6] have reviewed the HPCL, GC and i.r. methods employed for estimation of total aromatics in petroleum products and synfuels boiling in the kerosene range and have reported a faster and accurate i.r. method for estimating total aromatics in kerosene using 1600 cm^{-1} band due to C=C ring breathing mode of vibration and aromatic concentrate of similar characteristics as reference. In order to overcome the limitations[6] of the above method, the i.r. bands in the region 900–700 cm^{-1} due to out-of-plane C—H bending vibrations, which are characteristics of isomeric distribution of aromatics, together with 1600 cm^{-1} band in aromatic concentrates from kerosene fractions of different origins have been used to develop mathematical equations employing multiple regression analysis for estimation of total aromatics (vol %) in kerosene fractions and this is reported in the present paper.

2 EXPERIMENTAL

Aromatic concentrates, to be used as reference, from various kerosenes of varying origins, were separated on silica gel (Davison grade 923). The cut point was so monitored that there was no contamination of saturates in aromatics, although a slight amount of aromatics may go with saturates. The i.r. spectra of pure aromatic concentrates at different concentrations, in isooctane, were recorded on a Perkin–Elmer 399B infrared spectrophotometer in the 1800–1500 cm^{-1} and 900–700 cm^{-1} regions using 0·1 mm KBr cells and absorbance scale. The absorbances were measured at 1610, 810, 785, 745 and 705 cm^{-1} using baselines between 1630 and 1560 cm^{-1} and 830 and 690 cm^{-1} in the respective regions. The i.r. spectra of a few samples of kerosene fractions as such were recorded in these regions to check the applicability/accuracy of derived equation by comparing with FIA data. The multiple regression analysis of concentration (vol %) and aromatic absorbances at 1610, 810, 785, 745 and 705 cm^{-1} was done on a Hewlett Packard desk top computer.

3 RESULTS AND DISCUSSION

Using 60 concentrations in the range of 10–45 vol% of aromatic concentrates derived from kerosene fractions of crude oils obtained from different origins, a linear expression of the following form has been developed through multiple regression analysis involving absorbances per 0·1 mm path length at analytical wavenumbers and vol % concentration of aromatics:

$$C\ (\text{vol\%}) = -1{\cdot}627 + 4{\cdot}317\ A_{1610} + 3{\cdot}564\ A_{810} - 1{\cdot}138\ A_{785} \qquad (1)$$

At first, all the five bands (1610, 810, 785, 745 and 705 cm^{-1}) characteristic of aromatic structures were used in the regression analysis. However, after applying the criteria of maximum R (correlation coefficient), maximum F value, minimum σ (standard deviation) and minimum ESS (sum of squares of residuals), the final

TABLE 1

Accuracy of Total Aromatics Data Determined by i.r. Method

Sample No.	*Concentration of total aromatics (vol %)*		*Percentage of deviation*
	Standard sample	*By i.r.*	
1	18·90	18·34	+2·96
2	28·35	28·74	−1·38
3	14·18	14·58	−2·82
4	13·84	13·76	+0·57
5	21·79	21·13	+3·03
6	32·68	31·02	+5·08

expression [equation (1)] has been obtained based on absorbances at 1610, 810 and 785 cm^{-1} only. The deletion of independent variables is based on the t-values of 95% confidence level for a particular degree of freedom. The correlation coefficient of the final equation (1) thus obtained is found to be 0·9905.

The accuracy of the proposed method is shown in Table 1 by estimating the total aromatics in synthetic mixtures prepared by aromatics concentrates separated from various kerosene fractions. The data shows the accuracy of the method is within ±5% of the value of the standard sample prepared. The repeatability of the i.r. method based on quadruplicate estimations of kerosene fractions is found to be of the order of 4% (see Table 2).

Table 3 presents the comparison of the estimated values of total aromatics in different kerosene fractions by proposed i.r. method with those obtained by the FIA method. The percentage deviations of the proposed i.r. method from the FIA values are within about 5·5%.

The numerical constants in the derived equation are generally dependent on the particular instrument used. Although measured absorbance values (A-values) vary between spectrophotometers, there is a considerably smaller variation between A-

TABLE 2

Repeatability of the Proposed i.r. Method for the Determination of Total Aromatics in Kerosene Fractions

Sample No.	*Concentration of total aromatics (vol %)*					*Standard deviation*	*Coefficient of variation*
					Average value		
1	42·40	41·31	40·26	42·21	41·55	0·980	2·36
2	25·83	26·09	24·55	27·22	25·92	1·096	4·23
3	16·79	15·88	17·10	—	16·59	0·634	3·82

TABLE 3
Comparison of Total Aromatics of some Typical Kerosene Fractions by Infrared with FIA Method

Sample No.	*Boiling range*	*Concentration of total aromatics (vol %)*		*Percentage deviation*
		FIA	*i.r.*	
1	138–250	24·00	24·64	−2·67
2	140–270	24·70	25·49	−3·20
3	140–250	20·40	19·88	+2·55
4	140–250	24·30	24·55	−1·03
5	140–240	37·50	39·55	−5·47
6	140–250	37·20	38·06	−2·31
7	140–270	37·00	38·45	−3·92
8	175–265	22·10	22·85	−3·39

ratios in the same spectrum. Equation (1) may be rewritten as

$$C\ (\text{vol}\,\%) = X + Y\,(\text{A}_{1610} + 0{\cdot}826\ \text{A}_{810} - 0{\cdot}264\ \text{A}_{785}) \qquad (2)$$

where the constants X and Y are instrument-dependent. The weighting factors 0·826 and −0·264 are instrument-independent. Thus any instrument can be 'calibrated' with a few samples of known aromatics content; thus the constants X and Y can be determined.

4 CONCLUSION

The total aromatics content in kerosene fractions of crude oils can be quickly and accurately determined using a regression equation (2), which utilizes the absorbances of the characteristic i.r. bands in the 1600 cm^{-1} and 900–700 cm^{-1} regions. The accuracy of the method, when compared with standard samples is ±5%. When compared to the FIA method the deviation is found to be within 5·5%. The proposed method is applicable in the concentration range 10–45 vol% of total aromatics.

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