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Determination of boiling point of petrochemicals by gas chromatography–mass spectrometry and multivariate regression analysis of structural activity relationship



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ABSTRACT

Accurate understanding of analyte boiling points (BP) is of critical importance in gas chromatographic (GC) separation and crude oil refinery operation in petrochemical industries. This study reported the first combined use of GC separation and partial-least-square (PLS1) multivariate regression analysis of petrochemical structural activity relationship (SAR) for accurate BP determination of two commercially available (D3710 and MA VHP) calibration gas mix samples. The results of the BP determination using PLS1 multivariate regression were further compared with the results of traditional simulated distillation method of BP determination. The developed PLS1 regression was able to correctly predict analytes BP in D3710 and MA VHP calibration gas mix samples, with a root-mean-square-%-relative-error (RMS%RE) of 6.4%, and 10.8% respectively. In contrast, the overall RMS%RE of 32.9% and 40.4%, respectively obtained for BP determination in D3710 and MA VHP using a traditional simulated distillation method were approximately four times larger than the corresponding RMS%RE of BP prediction using MRA, demonstrating the better predictive ability of MRA. The reported method is rapid, robust, and promising, and can be potentially used routinely for fast analysis, pattern recognition, and analyte BP determination in petrochemical industries.

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1. Introduction

Crude petroleum is a complex mixture containing petrochemicals of wide range boiling point (BP) distributions. The utility of petroleum is highly dependent on its BP, necessitating the need for the development of analytical techniques, capable of crude oil separation into its various components. Separation of crude petroleum typically involves a conventional fractional distillation (FD) technique based on differences in petrochemicals BP distribution. Unquestionably, the determination of petrochemical BP distribution using conventional FD strategy is useful and critical. However, FD has significant challenges and drawbacks including, large sample size requirement, lengthy analysis time, and relatively poor accuracy. The drawbacks of FD has resulted in the current use of a simulated distillation using gas chromatography (GC) analysis as a better alternative strategy for petrochemical BP distributions determination in oil and gas industries [1–10].

Determination of BP of unknown sample using GC simulated distillation approach involves a two-step procedure. In the first

step, the unknown sample is co-separated with standards calibration mixture of known BP using GC. In the second step, a calibration curve involving the plot of BP of the standard calibration mixture versus analyte retention times is constructed. The constructed calibration curve is then subsequently used to evaluate the BP of the unknown sample. The determination of BPs distribution of petrochemicals using simulated distillation technique is not only simple and effective, but it is also rapid and requires a relatively small sample size. In addition, this strategy has been very effective and robust, with a reasonable BP prediction error. This technique has become routine for simulation of petrochemical's BP in the oil and gas industries.

The simulated distillation approach only focused on the use of ordinary univariate regression analysis (URA) of BP and analyte retention times. However, the similarities and/or differences in petrochemical structural activity relationship (SAR) could preclude the use of URA for accurate determination of BP distribution solely from GC retention times. For instance, analyte retention time is not always linearly related with BP, especially for analytes with extremely low or high boiling points. Besides, analyte SAR, including the shape, size, molecular weight, number of carbons, number of hydrogens, number of single bond, number of double bond, number of benzene ring, and the presence of other functional groups may

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have notable influence, not only on analyte retention times, but also on analyte elution order. In addition, analyte flash point, refractive index, density, and melting point may affect both the analyte retention times and elution order, hindering the use of URA for accurate BP prediction.

In this study, we hypothesized that, the use of simulated distillation from GC data in conjunction with multivariate regression analysis of petrochemicals structural activity relationship may provide a better alternative strategy to improve the accuracy of petrochemicals BP determination. The practical applications of MRA in conjunction with SAR for accurate prediction of analyte retention times of samples of petrochemical, pharmaceutical, and environmental interest have been demonstrated in chromatographic separation [11–15]. In a recent study, the potential utility of molecular weight, specific gravity, and cumulative weight fraction as inputs for artificial neural networks for the estimation of boiling point distributions of C_{7+} has also been demonstrated [16]. Unquestionably, the use of analyte molecular weight, specific gravity and cumulative weight fraction structural activity relationship input are significant for the estimation of boiling point. However, other analytes structural activity relationship including density, melting point, number of carbon, number of hydrogen, number of single bonds, number of double bonds, number of benzene rings, flash point, and refractive index may have considerable effects on the GC separation and/or petrochemical boiling point. This study therefore reported a comprehensive and the first combined use of a gas chromatography–mass spectrometry separation, analyte structural activity relationship, and multivariate analysis for the determination of petrochemicals BPs. The results of the BP analysis using MRA in this study were further compared with the results of a conventional simulated distillation method using univariate regression analysis of BP determination from GC data. Furthermore, the study explored the potential utility of analyte SAR in conjunction with MRA for petrochemical pattern recognition in GC separations.

2. Experimental

2.1. Material and chemical

Methanol, 2,2 dimethyl butane, hexene, benzene, 2,2,4 trimethyl pentane, n-heptane, toluene, p-xylene, n-nonane, n-decane, dodecane, n-tridecane, and n-tetradecane were obtained from Sigma-Aldrich. A Rtx-XLB column, D3710, and MA VPH calibration mix samples were purchased from Restek, Bellefonte, PA, USA. The chemicals used for the study were ACS certified grade or better purity.

2.2. GC separation and multivariate data analysis

A boiling point calibration mixture sample consisting of a 0.05% v/v of 2,2-dimethyl butane, hexene, benzene, 2,2, 4 trimethyl pentane, n-heptane, toluene, p-xylene, n-nonane, n-decane, dodecane, n-tridecane, and n-tetradecane was prepared in HPLC grade methanol. The analytes in the calibration mixture were chosen for the study because of variation in their structural activities relationship (SAR). A 1 μ L aliquot of the calibration mixture sample was directly injected and separated using a GC instrument equipped with a mass-spectrometer detector (GCMS-QP5000, Shimadzu). The GC separation was performed in a Rtx-XLB column (inner diameter: 0.25 mm; film thickness: 0.25 μ m; and length 30 m). The GC separation was performed in a temperature programming mode to ensure better analyte resolution. The column temperature was operated in a gradient programming mode, with an initial temperature of 33 $^{\circ}$ C, held for 3 min at 33 $^{\circ}$ C and then increased at the rate of 1 $^{\circ}$ C min^{-1} to 100 $^{\circ}$ C. The temperature was then held for 4 min at 100 $^{\circ}$ C, and then increased at a rate of 10 $^{\circ}$ C min^{-1} to 200 $^{\circ}$ C. Helium (He) gas was used as the mobile phase, with a column injection pressure of 52.1 kPa, a total flow of 30 mL min^{-1} , column flow of 1.1 mL min^{-1} , linear velocity of 37.6 cm s^{-1} , and a split ratio of 25:1. The GC–MS interface temperature was set at 300 $^{\circ}$ C. The mass spectrometer detector was operated in a scan acquisition mode, scanning from 40 m/z to 400 m/z . Each analyte peak in the calibration mixture GC chromatogram was identified and confirmed using the mass spectrometer.

2.3. Analyte structural activity relationship and multivariate regression analysis

A partial-least-square (PLS1) multivariate regression analysis was used to correlate changes in analyte structural activity relationships and corresponding retention times from GC separation with analyte BP in the calibration mixture. Table 1 shows the analyte structural activity relationship and GC retention time data set used for PLS1 regression model development. The PLS1 model was carefully optimized and subsequently used to predict analyte BPs in two commercially available calibration gas mix samples (D3710 and MA VHP). Multivariate data analysis was performed using chemometric software (9.8, The Unscrambler, CAMO Incorporation, NJ).

3. Result and discussion

3.1. GC separation and multivariate regression analysis

Fig. 1 shows the chromatogram of the GC analysis of the calibration mixture sample. Obviously, all analytes in the mixture

Table 1
Structural activity relationship of calibration petrochemical mixtures data set for multivariate analysis.

Analyte	D (g mL^{-1})	MP ($^{\circ}$ C)	MW (g mol^{-1})	# SB	# DB	# C	# H	RI	VD	FP ($^{\circ}$ C)	BP ($^{\circ}$ C)	RT (min)
2,2 Dimethyl butane	0.6490	−100	86.18	19	0	6	14	1.369	2.97	−29	50	1.377
Hexene	0.6780	0	84.16	16	1	6	12	1.388	3	−25	63	1.652
Benzene	0.8740	5.5	78.11	9	3	6	6	1.5	2.77	−11	80	2.211
2,2,4 Trimethyl pentane	0.6920	−107	114.23	25	0	8	15	1.39	3.9	−12	99	2.522
n-Heptane	0.6840	−91	100.2	22	0	7	16	1.387	3.5	−4	98	2.709
Toluene	0.8650	−93	92.14	12	3	7	8	1.496	3.2	4	111	3.948
p-Xylene	0.8610	13	106.17	11	3	8	10	1.495	3.7	25	139	6.635
n-nonane	0.718	−53	128.26	28	0	9	20	1.405	4.41	31	151	7.617
n-Decane	0.7300	−30	142.28	31	0	10	22	1.411	4.9	46	174.1	10.763
Dodecane	0.7500	−9.6	170.33	37	0	12	26	1.421	5.96	74	216.3	15.357
n-Tridecane	0.7560	−5.3	184.36	40	0	13	28	1.425	6.4	94	234	17.003
n-Tetradecane	0.7620	5.5	198.39	43	0	14	30	1.429	6.83	100	253	18.978

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