



Isothermal Kováts retention indices of sulfur compounds on a poly(5% diphenyl–95% dimethylsiloxane) stationary phase[☆]

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Abstract

Isothermal Kováts retention indices of 21 sulfur compounds relevant to the fuel gas and food industries are reported on a poly(5% diphenyl–95% dimethylsiloxane) capillary column stationary phase. Measurements were performed at four temperatures and the temperature dependence of the values modeled with Antoine-type equations. Indices were calculated using a non-linear technique, and the predicted values were found to agree with values obtained using traditional logarithmic predictions. We demonstrate that there is sufficient separation between retention indices to predict the identity of a compound by its retention index.

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Keywords: Retention indices; Organic sulfur compounds; Sulfides; Thiols

1. Introduction

Sulfur compounds play an important role in many industries, including the food and petrochemical industries. Sulfur compounds are an important part of many aromas in food and beverages, including wine and beer [1]. In the petrochemical industry, sulfur compounds not only occur naturally, but also are used as odorants in fuel gases to warn consumers of fuel leaks. Accurate identification of these compounds in a wide range of matrices is very important, and relies heavily on the predictive capability of

metrology such as gas chromatography (GC). Retention parameters obtained from chromatographic applications are fundamental data that provide important information not only in the identification of chromatographic peaks, but also in the development of separation and quantitation strategies. Knowledge of these retention properties on various stationary phases provides the analyst with a suite of analytical options to aid in development techniques. A widely accepted method of reporting retention parameters in gas chromatography is the retention index system developed by Kováts [2].

The importance of sulfur compounds in various industry sectors has led to studies and databases of retention indices for these compounds have been reported [3–6]. None, however, have reported data over a significant temperature range. In this paper, we report the isothermal retention indices for a series

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of sulfur compounds obtained from a regression technique, and temperature-dependent models for measured indices. The measurements are made on a common gas chromatographic stationary phase using a capillary gas chromatographic system, equipped with a dual detection system comprised of flame ionization detection (FID) and sulfur chemiluminescence detection (SCD) systems.

2. Theory

Isothermal Kováts retention indices can be calculated by a logarithmic interpolation using simple retention parameters. This relationship is expressed by:

$$I(T) = 100 \cdot \left[\frac{\log X_S - \log X_n}{\log X_{n+1} - \log X_n} + n \right] \quad (1)$$

where the isothermal retention index at temperature T , $I(T)$, is a function of the retention factor, X , for the solute (S) and two n -alkane standards. The alkane standards, represented by carbon numbers n and $n+1$, are selected such that their retention factors bracket the retention factor X_S of the solute (i.e. $X_n < X_S < X_{n+1}$). Various retention factors can be used in Eq. (1) including adjusted retention time, t'_R , net retention volume, V_N , and specific retention volume, V_g .

Inherent to Eq. (1) is the assumption that the relationship between the logarithmic value of the retention factor and the retention index is linear. Indeed, an ideal linear relationship is always assumed in application of Eq. (1) since the retention factors of only two n -alkanes determine this relationship. Variation in individual retention times of the n -alkanes is however a potential source of error in determining retention indices. Thus, various graphical and regression techniques have been suggested to reduce the error in these calculations [7–12].

Recent research has demonstrated that the relationship between the retention time, t_R , and the carbon number of n -alkanes is represented by the expression:

$$t_R(n) = a + \exp(b + cn^d) \quad (2)$$

where the coefficients a , b , and c are coefficients

obtained from the fit and n is the carbon number of a n -alkane [8–12]. The coefficient d accounts for the observed non-linearity in the semi-log plot between the logarithm of retention time and n -alkane carbon numbers [10,12]. Using retention data from a series of n -alkanes, the coefficients in Eq. (2) can be determined by non-linear regression, and used in the calculation of isothermal retention indices for additional compounds by:

$$I_S(T) = 100 \cdot \left(\frac{[\log(t_{R,S} - a)] - b}{c} \right)^{\frac{1}{d}} \quad (3)$$

In this paper, we have chosen to use Eq. (3) in the calculation of the retention indices of the sulfur compounds.

The utility of chromatographic databases with retention indices can be enhanced if knowledge of the temperature dependence of each retention index is incorporated into the data sets. It is known that the temperature dependence of retention indices follows a hyperbolic form that can be represented by the Antoine-like equation:

$$I_S(T) = A + \frac{B}{T + C} \quad (4)$$

where A , B , and C are empirically determined constants and T is the thermodynamic temperature. If sufficient data are available, the constants are determined using non-linear regression techniques. At a minimum, the retention indices at three different temperatures must be used to estimate the coefficients. Examples of applications in which this approach has been used are detailed elsewhere [13,14]. Moreover, retention indices often show significant linearity over a certain temperature range. Thus, it is often of value to report the temperature dependence as a slope coefficient, $\delta I / 10^\circ\text{C}$, the variation of I of a particular solute on a stationary phase over a temperature change of 10°C [13].

3. Experimental

All sulfur fluids and n -alkane standards used were of research grade, ranging in purity from 92 to 99.9% (mass/mass). All were obtained from commercial sources and used without further purification.

Dry, research-grade nitrogen was used as the carrier gas for all chromatographic measurements. Research-grade hydrogen and oxygen were used for SCD. Research-grade hydrogen and air generated with a catalytic “zero-air” module were used for FID.

3.1. Equipment and apparatus

Retention time measurements were performed on a commercially available gas chromatograph equipped with a split/splitless injector, automatic sampler and electronic flow control. The effluent of the column was split (5:1) between the FID and SCD systems. Column head pressure was maintained at 138 kPa above ambient pressure (20 p.s.i.g.) for all measurements (1 p.s.i. = 6894.76 Pa). Isothermal measurements were made at four different column temperatures (60, 80, 100, and 120 °C).

A commercially available poly(5% diphenyl–95% dimethylsiloxane) capillary column was used to obtain all chromatograms. The column was 30 m in length with an internal diameter (I.D.) of 250 μm and the stationary-phase film thickness was 0.1 μm . *n*-Decane was used as the solvent for all sulfur solutes. Solute concentration in the sample was adjusted such that Gaussian peak shapes were obtained for the analyte in SCD. The retention time for each solute was measured by injecting 1- μl liquid samples. All samples were injected with the automatic sampler in triplicate, into a split–splitless injector set with a split ratio of 200:1. The injector and FID system were maintained at 250 °C. Hydrogen flow to the FID system was 1.5 ml/min. The inlet of the SCD system was held at 150 °C and the reaction chamber was maintained at 975 °C. Hydrogen, oxygen, and ozone flows in the SCD system were 260, 5.5, and 25 ml/min, respectively. Seven *n*-alkane standards (*n*-pentane through *n*-undecane) were measured at 60 °C and eight *n*-alkane standards (*n*-pentane through *n*-dodecane) were measured at the three higher column temperatures. Retention time data were collected on a commercial computer equipped with peak processing software.

3.2. Retention index calculations

Since SCD operates at a vacuum (~ 0.133 Pa in the

photocell), retention times measured by SCD and FID are offset. Thus, retention times from SCD cannot be directly used for calculation of the retention indices. Most of the sulfur compounds, however, had detectable FID signals that enabled a time offset correction to be calculated at each temperature. This offset correction, t_{offset} , was determined by performing a linear regression between the measured retention times from FID and SCD as follows:

$$t_{\text{R,FID}} = t_{\text{R,SCD}} + t_{\text{offset}} \quad (5)$$

where $t_{\text{R,FID}}$ is the retention time from FID and $t_{\text{R,SCD}}$ is the retention time from SCD, for a particular sulfur compound. The $t_{\text{R,FID}}$ for all sulfur compounds were then calculated at each temperature by application of Eq. (5).

Retention indices were also calculated using Eq. (1) to compare to the fitted values obtained from Eq. (3). Corrected retention times, t'_{R} , were used as the retention parameters in Eq. (1). The coefficient “*a*” from Eq. (3) is an approximation of the hold-up time. For this portion of the study, however, a retention index calculation that was completely independent of Eq. (3) was needed to objectively evaluate the difference in the two calculation methods. Thus, the hold-up time for the capillary column at each temperature was calculated using the Ambrus method [15]. Regression analyses were performed using a commercially available statistical software package.

4. Results and discussion

The Kováts retention indices for the 21 sulfur compounds studied are listed in Table 1 for four different temperatures. The measurement uncertainties for the reported values were calculated from the standard error of the regression obtained from Eq. (3), and are included with each measurement (with a coverage factor $k = 2$; that is, 2 SD). The linear slope, $\delta I/10$ °C, calculated over the temperature range of the measurements, is also included in Table 1. These values were obtained by performing a linear regression of *I* against the temperature range of the study (i.e. 333.15–393.15 K).

The indices reported in Table 1 show an average

Table 1
Kováts retention indices for sulfur compounds measured on poly(5% diphenyl–95% dimethylsiloxane) stationary phase GC column

Analyte	Retention index ^a				$\delta I/10\text{ K}$
	60 °C (333 K)	80 °C (353 K)	100 °C (373 K)	120 °C (393 K)	
Ethanethiol	517.4±0.6 0.2%	514.2±0.5 0.1%	512.6±2.5 0.5%	528.5±4.1 0.8%	1.6
Methyl sulfide	532.0±0.6 0.2%	530.2±0.4 0.1%	533.7±2.1 0.4%	543.6±3.8 0.7%	1.9
Carbon disulfide	558.0±0.6 0.2%	557.3±0.4 0.1%	564.4±1.8 0.3%	576.0±3.6 0.6%	3.1
2-Propanethiol	565.9±0.6 0.2%	569.0±0.4 0.1%	572.1±1.8 0.3%	581.7±3.7 0.6%	2.5
2-Methyl-2-propanethiol	599.2±0.6 0.2%	602.5±0.4 0.1%	605.5±1.8 0.3%	617.0±3.7 0.6%	2.8
1-Propanethiol	615.4±0.6 0.2%	615.7±0.4 0.1%	617.0±1.8 0.3%	630.0±3.7 0.6%	2.3
Methyl ethyl sulfide	618.8±0.6 0.2%	621.9±0.4 0.1%	625.0±1.8 0.3%	638.2±3.7 0.6%	3.1
1-Methyl-1-propanethiol	669.4±0.6 0.2%	672.6±0.4 0.1%	677.2±1.7 0.3%	688.8±3.3 0.5%	3.1
Thiophene	674.6±0.5 0.2%	679.6±0.4 0.1%	686.1±1.7 0.2%	700.0±3.2 0.5%	4.1
2-Methyl-1-propanethiol	680.1±0.5 0.2%	683.4±0.4 0.1%	687.8±1.7 0.2%	700.0±3.2 0.5%	3.2
Ethylsulfide	700.4±0.5 0.1%	703.7±0.3 0.04%	708.5±1.6 0.2%	717.9±3.1 0.4%	2.9
1-Butanethiol	714.8±0.5 0.1%	716.9±0.3 0.04%	721.3±1.5 0.2%	729.7±2.9 0.4%	2.5
Methyl disulfide	747.1±0.5 0.1%	751.3±0.3 0.04%	758.5±1.4 0.2%	767.8±2.7 0.4%	3.5
Tetrahydrothiophene	806.3±0.5 0.1%	812.6±0.3 0.04%	821.0±1.4 0.2%	832.5±2.5 0.3%	4.4
1-Pentanethiol	814.0±0.5 0.1%	817.0±0.3 0.04%	821.7±1.4 0.2%	828.8±2.5 0.3%	2.5
Allyl sulfide	856.2±0.5 0.1%	860.3±0.3 0.03%	864.6±1.4 0.2%	871.6±2.7 0.3%	2.5
Propylsulfide	884.8±0.5 0.1%	887.4±0.3 0.03%	891.2±1.5 0.2%	896.7±2.7 0.3%	2.0
1-Hexanethiol	912.5±0.5 0.1%	916.4±0.3 0.03%	920.9±1.5 0.2%	927.3±2.8 0.3%	2.4
Butyl sulfide	1078.1±0.6 0.1%	1081.3±0.3 0.03%	1084.4±1.4 0.1%	1088.5±2.6 0.2%	1.7
Propyl disulfide	1098.0±0.7 0.1%	1104.6±0.3 0.03%	1110.9±1.4 0.1%	1118.4±2.7 0.2%	3.4
Butyl disulfide	NA	NA 0.3%	1298.2±4.4 0.7%	1307.2±8.9	NA

^a Retention indices reported with error and RSD.

uncertainty (2 SD) of 1.6 retention units. This average is somewhat higher than those reported previously [14]. Two points, however, should be noted. First, the average uncertainty at lower temperatures (i.e. 333.15 and 353.15 K) is 0.5 retention units, with the higher temperatures showing a larger degree of measurement uncertainty. This is expected, since the compounds are eluting off the column faster, resulting in an increased uncertainty. Second, solute-stationary phase interactions need to be considered to place the reported uncertainty values in context. Reported precision values, expressed in standard deviations, typically range from 0.02 to 0.05 retention indices units for hydrocarbons on non-polar stationary phases [13,16]. The polar sulfur compounds in this study are interacting with a non-polar stationary phase. It is known that measurement uncertainty of non-polar compounds increases with an increase in the polarity of the stationary phase

[17]; thus, the moderate increase observed in measurement uncertainty with the data reported here would be expected.

The dependence of retention index on temperature is shown graphically in Fig. 1 for each sulfur compound. For presentation purposes, the compounds have been grouped together by functional group. All compounds exhibit a positive slope, indicating higher retention indices with an increase in temperature. This is a characteristic commonly observed in most, but not all compounds [14].

The data given in Table 1 and graphically shown in Fig. 1 indicate that the solutes are not following a simple linear relationship with temperature. Thus, the $\delta I/10\text{ }^\circ\text{C}$ values in Table 1 do not adequately represent the data over the measured temperature range. A more appropriate representation of the hyperbolic nature of the data can be expressed through application of Eq. (4). The fitted coefficients to the Antoine-

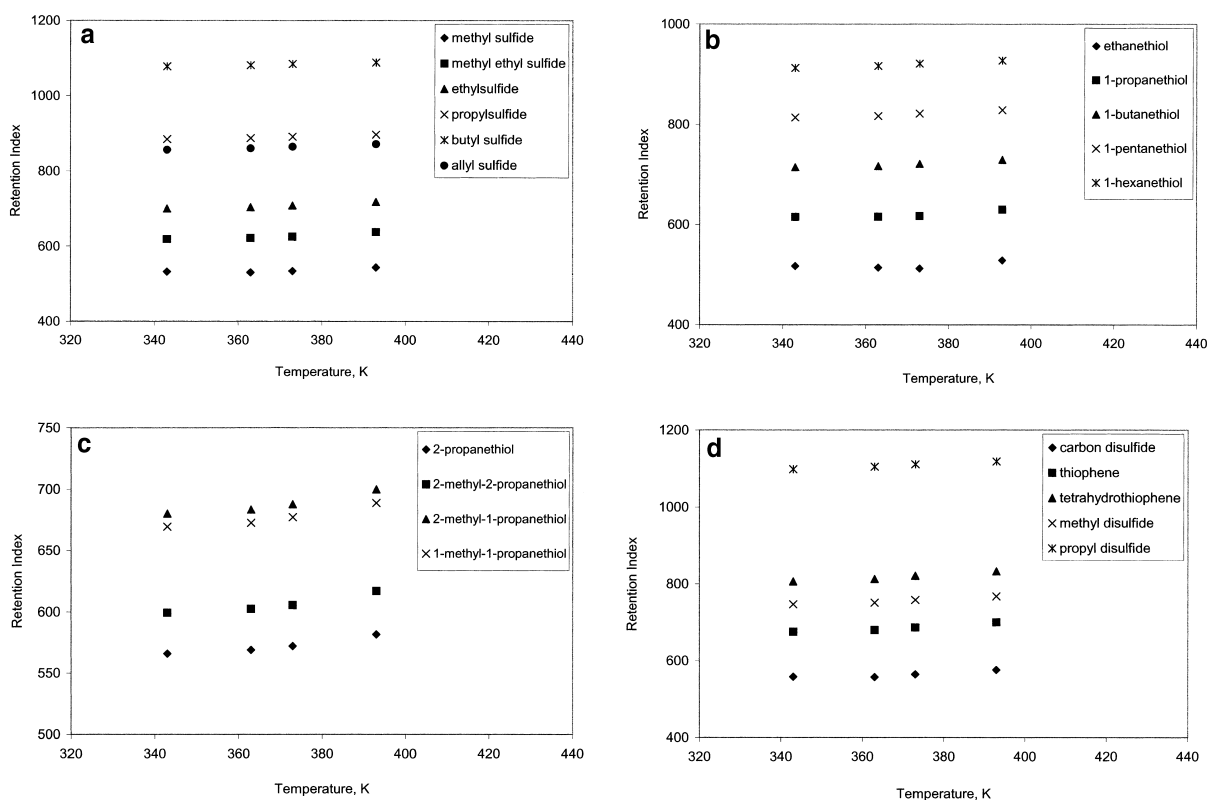


Fig. 1. Kováts retention indices as a function of temperature for the sulfur compounds reported in this study. Retention indices are grouped in chemical classes by sulfides (a), linear thiols (b), branched thiols (c), and disulfides and cyclic sulfides (d).

Table 2

Coefficients from the non-linear fits to Antoine-type equation for each sulfur compound measured on poly(5% diphenyl–95% dimethylsiloxane stationary phase GC column

Compound name	I_{average}	A	B	C	Average residual
Ethanethiol	518.2	517.6	70.7	−386.7	0.89
Methyl sulfide	534.8	529.5	−98.4	−400.1	0.98
Carbon disulfide	563.9	549.9	−570.9	−415.0	1.28
2-Propanethiol	572.2	558.5	−691.6	−423.0	0.37
2-Methyl-2-propanethiol	614.2	596.3	−231.3	−397.5	0.64
1-Propanethiol	619.5	614.4	−59.7	−397.0	0.07
Methyl ethyl sulfide	625.9	613.2	−472.9	−412.1	0.45
1-Methyl-1-propanethiol	677.0	659.5	−914.5	−424.4	0.16
Thiophene	685.1	656.5	−1905.6	−436.9	0.26
2-Methyl-1-propanethiol	687.8	671.1	−815.9	−421.4	0.26
Ethylsulfide	707.6	686.9	−1429.3	−439.3	0.08
1-Butanethiol	720.6	705.3	−907.0	−430.4	0.14
Methyl disulfide	756.2	717.4	−4267.3	−477.6	0.24
Tetrahydrothiophene	818.1	759.3	−7863.3	−500.5	0.00
1-Pentanethiol	820.4	796.4	−2277.4	−463.4	0.07
Allyl sulfide	863.2	828.9	−4621.5	−501.6	0.23
Propylsulfide	890.0	868.6	−2279.7	−474.3	0.00
1-Hexanethiol	919.3	882.8	−5430.7	−515.3	0.11
Butyl sulfide	1083.1	1033.0	−14 602.5	−656.3	0.11
Propyl disulfide	1108.0	903.1	−124 544.0	−971.8	0.20

type hyperbolic representation of the data are shown in Table 2. The values were obtained using a non-linear regression (Levenberg-Marquardt) iterative method, with starting values obtained using methods detailed previously [14]. In addition, the average retention index, I_{average} , over the temperature range measured is also included in Table 2. I_{average} is useful as a diagnostic tool in evaluating the fitted coefficients from the Antoine equation. The values for I_{average} and the fitted coefficient “A” should be relatively close to one another. If they are not, it is possible that the values for the coefficients represent a local minimum in the Antoine-type non-linear fit. The average residuals for each fit, expressed in retention units, I , are also included in Table 2. Residual values ranged from 0 to 1.28 I , with an overall average residual of 0.33. The highest residuals, and thus greatest uncertainties, are observed in compounds that elute from the column quickly (e.g. $t_{\text{R}} = 0.035$ min). The highest residual of 1.28 I corresponds to carbon disulfide, the single analyte that has no FID response.

An additional item to note is the ability of the method presented here to measure the retention

indices of carbon disulfide. Unlike the other compounds studied here, carbon disulfide is not detectable by FID. By using dual-detection (FID/SCD), however, it is possible to determine the retention index of compounds without FID signals.

Consideration of error contributed from using retention times calculated with the detector offset was also evaluated. For a vast majority of the analytes, the offset does not significantly contribute to error in the retention indices calculation. For example, at the high temperature (120 °C), where the error in calculated retention index would be expected to be larger, the fit of the SCD signal with the FID signal results in a standard error of prediction of 0.001 min in the corrected retention time. Using the error in the regression analysis, this propagates to an average error of 2.5 I units with one significant outlier. If this outlier is removed, the resulting error is reduced to 1.9 I units. It should also be pointed out the corrected FID signal and the actual measured FID signal of nearly 85% of the analytes measured at this temperature agree within 0.001 min. We choose to use the FID signal derived from SCD using the offset equation for two reasons. First, SCD has a

higher signal-to-noise ratio for the compounds in this study, and thus retention time determination should have a higher degree of precision from the SCD. Second, by calculating an offset, we can determine the retention index of compounds that have no FID signal.

To compare use of Eq. (3) in determining retention indices, indices for the complete set of retention data were also calculated using Kováts

approach [i.e. Eq. (1)]. This comparison is shown in Fig. 2, with the calculated difference between the predicted values plotted as a function of the retention index value from Eq. (3). The 95% confidence intervals for both the model and Kováts approach [Eq. (1)] are also included. For brevity, only comparisons at the two temperature extremes are shown. In general, the predicted values from both methods are in good agreement for compounds with retention indices of 600 or greater. As shown in Fig. 2a and b, the magnitude of the difference between the two methods (expressed in retention indices) is within the 95% confidence intervals for the retention indices predicted from Eqs. (1) and (3) for compounds with retention indices of 600 or greater. Thus, both methods are predicting the same values within the calculated uncertainty for each approach. This is in agreement with retention studies of hydrocarbons using this algorithm [11,12].

The deviation in the two methods for analytes with retention indices of 600 or less, as shown in Fig. 2, warrants further comment. First, low retention times will produce higher uncertainties in retention indices. At the two higher column temperatures (100 and 120 °C), less than 20% of the analytes had corrected retention times of less than 0.050 min. Using the model, uncertainty is predicted across all retention times. While this is conservative, we think it is appropriate. If error is propagated for values using the traditional Kováts approach, prediction error will vary with retention time. This is graphically illustrated in Fig. 2a and b. The question then becomes at what point is one approach a more accurate reflection on the data? For analytes with retention index below 600, it is not clear from the current data. It is, however, a very interesting question indeed, and one we are attempting to answer with a different study.

Databases of Kováts retention indices are useful in identifying compounds by gas chromatography. Thus, a logical test of the data was to determine whether all sulfur compounds could be distinguished from each other based on measured Kováts retention indices. In order to perform this evaluation in a systematic manner, the difference matrix between all the Kováts retention indices was calculated for the 20 sulfur compounds measured at 60 °C [14]. The resulting 20×20 matrix formed by calculating the absolute difference between each retention index is

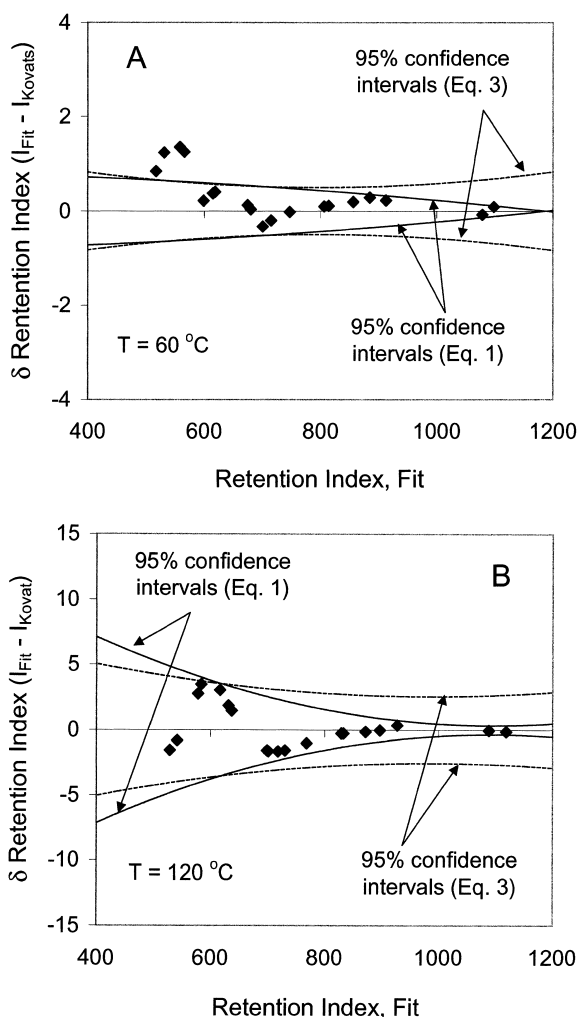


Fig. 2. Comparison of logarithmic and regression techniques for determining I . The calculated difference between I values determined by the regression technique [Eq. (3)] and Kováts' method [Eq. (1)] plotted against the value determined by regression technique at 60 °C (a) and 120 °C (b) is shown. The corrected retention time, $t'_{R,}$ is retention factor used in Eq. (1).

Table 3
Difference matrix between measured I at 60 °C for 20 sulfur-containing analytes

Analyte	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
Analyte I	517.4	532.0	558.0	565.9	599.2	615.4	618.8	669.4	674.6	680.1	700.4	714.8	747.1	806.3	814.0	856.2	884.8	912.5	1078.1	1098.0	
1	517.4	0.0																			
2	532.0	-14.6	0.0																		
3	558.0	-40.6	-26.0	0.0																	
4	565.9	-48.5	-34.0	-8.0	0.0																
5	599.2	-81.8	-67.2	-41.2	-33.3	0.0															
6	615.4	-98.0	-83.5	-57.5	-49.5	-16.2	0.0														
7	618.8	-101.4	-86.8	-60.8	-52.8	-19.6	-3.3	0.0													
8	669.4	-152.0	-137.4	-111.4	-103.4	-70.2	-53.9	-50.6	0.0												
9	674.6	-157.2	-142.6	-116.6	-108.7	-75.4	-59.2	-55.9	-5.2	0.0											
10	680.1	-162.7	-148.2	-122.2	-114.2	-80.9	-64.7	-61.4	-10.8	-5.5	0.0										
11	700.4	-183.0	-168.4	-142.4	-134.4	-101.1	-84.9	-81.6	-31.0	-25.7	-20.2	0.0									
12	714.8	-197.4	-182.8	-156.8	-148.8	-115.5	-99.3	-96.0	-45.4	-40.1	-34.6	-14.4	0.0								
13	747.1	-229.7	-215.1	-189.1	-181.1	-147.9	-131.6	-128.3	-77.7	-72.4	-66.9	-46.7	-32.3	0.0							
14	806.3	-288.9	-274.3	-248.3	-240.3	-207.1	-190.8	-187.5	-136.9	-131.7	-126.1	-105.9	-91.5	-59.2	0.0						
15	814.0	-296.5	-282.0	-256.0	-248.0	-214.7	-198.5	-195.2	-144.6	-139.3	-133.8	-113.6	-99.2	-66.9	-7.7	0.0					
16	856.2	-338.8	-324.2	-298.2	-290.3	-257.0	-240.8	-237.4	-186.8	-181.6	-176.1	-155.8	-141.4	-109.1	-49.9	-42.3	0.0				
17	884.8	-367.4	-352.8	-326.8	-318.8	-285.6	-269.3	-266.0	-215.4	-210.2	-204.7	-184.4	-170.0	-137.7	-78.5	-70.8	-28.6	0.0			
18	912.5	-395.1	-380.6	-354.6	-346.6	-313.3	-297.1	-293.8	-243.1	-237.9	-232.4	-212.2	-197.8	-165.5	-106.3	-98.6	-56.3	-27.7	0.0		
19	1078.1	-560.7	-546.2	-520.2	-512.2	-478.9	-462.7	-459.4	-408.8	-403.5	-398.0	-377.8	-363.4	-331.1	-271.9	-264.2	-221.9	-193.4	-165.6	0.0	
20	1098.0	-580.6	-566.0	-540.0	-532.1	-498.8	-482.6	-479.2	-428.6	-423.4	-417.9	-397.6	-383.2	-350.9	-291.7	-284.0	-241.8	-213.2	-185.5	-19.9	0.0

shown in Table 3 (butyl sulfide is not included in the data set since it did not elute at this temperature). As expected, the diagonal values are all zero, separating difference values that are mirror images of each other. For clarity, only one side of the difference values is shown (again, recognizing that the mirror image values are of opposite sign and equal magnitude). Assuming each chromatographic peak can be approximated with a Gaussian distribution, the retention time (and thus I) can be predicted with a confidence of 99.7% if a spread of six standard deviations (6σ) from the mean is assumed. We selected this as the go/no-go criterion, and calculated the criterion value based on the average standard deviations of each sulfur compound. This resulted in a calculated criterion of 1.5 units of I . Review of the data in Table 3 show that all difference values exceeded the criterion, with the smallest difference value being 3.3. Thus, all sulfur compounds measured in this study can be distinguished using Kováts retention indices at 60 °C. It should be noted that this prediction assumes the absence of a co-eluting sulfur compound. In the event that a non-sulfur containing compound co-elutes with a sulfur compound of interest, identification of the sulfur compound is still possible with SCD. On the other hand, co-eluting sulfur compounds prevent the positive identification of each of the sulfur compounds at one temperature using Kováts retention indices. It is a simple matter, however, to predict $I(T)$ that may allow for complete resolution (and thus, more reliable identification) of the co-eluting compounds by calculating retention indices at a second temperature using the temperature coefficients reported here.

5. Conclusion

Isothermal Kováts retention indices, on a common GC stationary phase, of 21 sulfur compounds relevant to the petroleum and food product industries have been presented at four temperatures. The retention indices are calculated using a non-linear algorithm, and are in excellent agreement with retention indices calculated using traditional logarithmic

approaches. Fitted coefficients, obtained from the measured data, are useful in predicting retention behavior for the measured sulfur compounds at temperatures other than those reported here.

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