

Thermal Conductivity Detector Analysis of Hydrogen Using Helium Carrier Gas and HayeSep® D Columns

Kirk Snavely and Bala Subramaniam*

Department of Chemical and Petroleum Engineering, University of Kansas, Lawrence, KS 66045

Abstract

The thermal conductivity detector (TCD) response of hydrogen using helium carrier gas is investigated to obtain a linear response in the 6–60% hydrogen concentration range. The study is conducted using a Hewlett-Packard 5890 Series II GC incorporating either one or two 1.83-m × 3.18-mm stainless steel columns packed with 80/100-mesh HayeSep® D. Replicate data are analyzed using an analysis of variance (ANOVA) for testing the linearity of regression. TCD response curves are generated for replicates of three sets of sample size and TCD temperature: 10 μ L and 130°C, 1 mL and 300°C, and 100 μ L and 140°C. The linearity is limited: 6–32.5% hydrogen and 32.5–66.9% hydrogen for 10 μ L, 6–50.3% hydrogen for 1 mL, and nonlinear for 100 μ L (0.82–8.7% hydrogen). These results are in sharp contrast to those of Villalobos and Nuss (1965), who report a linear response from 0 to 70% hydrogen with a 50- μ L sample. The nonlinear response observed in the present study is hypothesized to be due to better resolution obtained with the HayeSep D columns, producing taller peaks. Consequently, for a given sample size, the maximum concentration in the Gaussian peak surpasses the linear range of the hydrogen-in-helium TCD response, yielding concave-downward curves for small sample sizes.

Introduction

Thermal conductivity detectors (TCD) are often used in packed-column gas chromatography (GC). For the analysis of most gases, helium (He) is the carrier gas of choice. The large difference in thermal conductivity between He and other gases enhances the sensitivity of TCD detection and generally produces a linear response. However, the analysis of hydrogen (H_2) using He as a carrier gas presents a problem. Although the thermal conductivity of H_2 is greater than that of He, the thermal conductivity of the H_2 -He binary mixture is not a simple monotonic increasing function of H_2 concentration. Rather, the thermal conductivity goes through a local minimum at low concentrations of H_2 before increasing to the

pure H_2 value (1,2). This creates a potential for a nonlinear response.

Villalobos and Nuss (3) investigated the analysis of H_2 using a GC equipped with a TCD. Figure 1A shows qualitatively the relative TCD detector signal as a function of H_2 concentration in the He carrier gas. Figure 1B displays the H_2 peak shapes corresponding to the H_2 concentrations in Figure 1A (e.g., peak shape 1 corresponds to point 1 on the relative detector

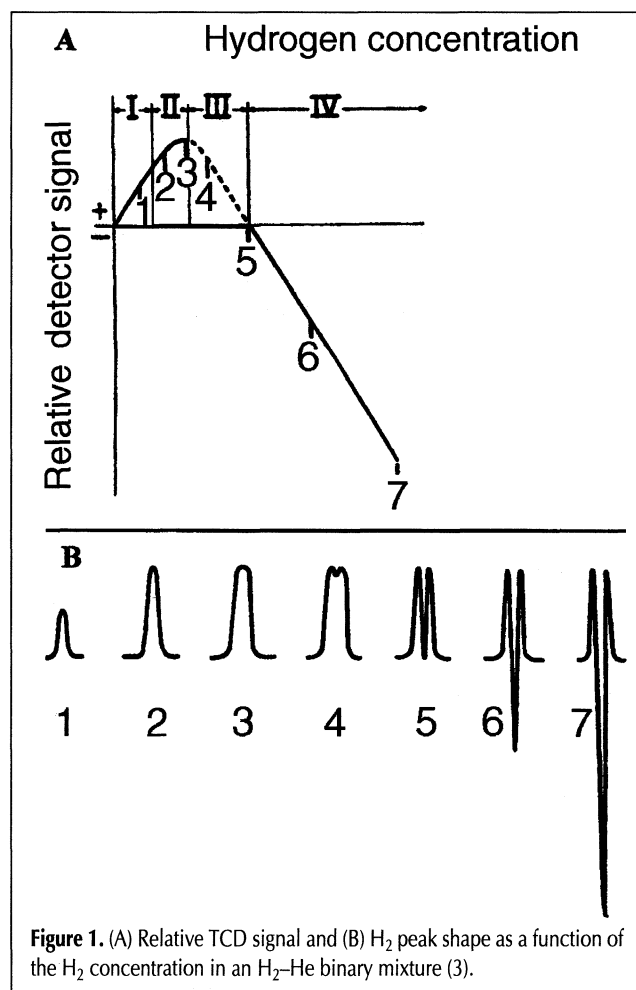


Figure 1. (A) Relative TCD signal and (B) H_2 peak shape as a function of the H_2 concentration in an H_2 -He binary mixture (3).

* Author to whom correspondence should be addressed.

signal curve). For H₂ concentrations in region I of Figure 1A, the peak is positive, and the TCD response (in terms of peak height) is linear.

The current investigation was part of the development of a GC method for the analysis of Fischer-Tropsch synthesis products and reactants. Helium was desirable for use as a carrier gas to increase the TCD sensitivity for detection of CO, CH₄, CO₂, and H₂O in the reactor effluent. The goal was to obtain a linear TCD response to H₂ in the concentration range of 6–60% using He as a carrier gas. Peak area rather than peak height responses

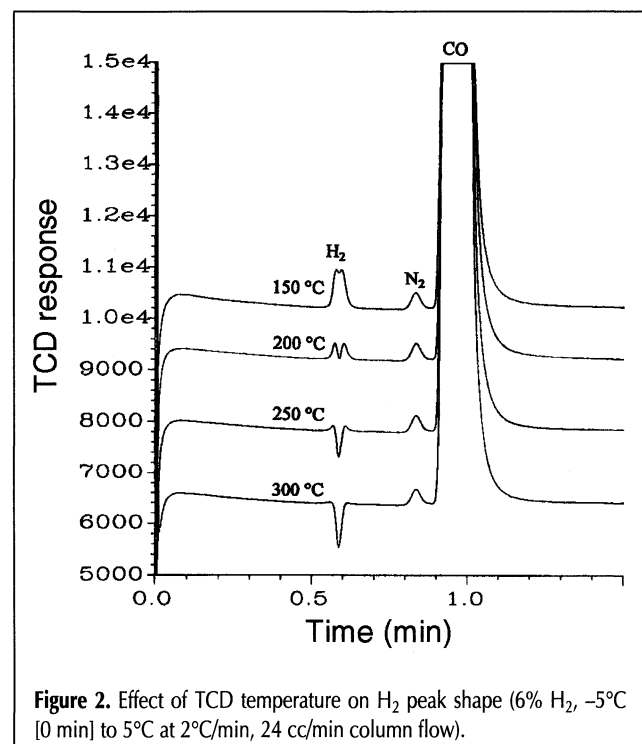


Figure 2. Effect of TCD temperature on H₂ peak shape (6% H₂, -5°C [0 min] to 5°C at 2°C/min, 24 cc/min column flow).

were used in the present study because peak area response curves are more linear than peak height response curves (1,4). To accomplish this goal, parameters such as oven and detector temperatures and sample size were adjusted to operate in either region I or region IV of Figure 1A.

Experimental

Materials

Gas standards used in the study were as follows: a custom 18-component mixture containing permanent gases (including 6% H₂ and 6% CO) and hydrocarbons for general use with the Fischer-Tropsch product analysis (Matheson, Joliet, IL), 10.2% H₂ in N₂ (Scott Specialty Gases, Troy, MI), 32.5% H₂ in CO, 49.7% CO in H₂, and 33.1% CO in H₂ (Air Products and Chemicals, Lenexa, KS). The industrial-grade He used as a carrier gas, obtained from Air Products and Chemicals, flowed through a high-capacity gas purifier (Supelco catalog #2-3800, Bellefonte, PA) prior to entering the GC.

Equipment

A Hewlett-Packard 5890 Series II GC (Palo Alto, CA) incorporating either a single 1.83-m × 3.18-mm stainless steel column (packed with 80/100 mesh HayeSep® D) or two of these columns in series was used for the analyses. Data were acquired and integrated using Hewlett-Packard 3365 Chemstation software. Analytical conditions, unless otherwise noted, are given in Table I. For analyses using a single column, TCD response curves for H₂ were generated by sampling several gas standards at atmospheric pressure, using atmospheric balancing during sampling in order to obtain repeatable samples.

The sample gas flow through the sample loop was shut off for 20 s prior to making an injection in order to equilibrate the sample loop contents with atmospheric pressure. Concentrations were normalized to 760 mm Hg. For the configuration of two columns placed in series, low H₂ concentrations were studied. It was convenient to generate TCD response curves for H₂ by sampling a single gas standard under various degrees of vacuum (1). When a different custom-prepared gas standard containing H₂ was analyzed at atmospheric pressure in order to test the quantitative analysis, the concentration of H₂ calculated from the calibration curve (generated using this vacuum technique) proved to be accurate (5).

The temperature program was influenced by the capillary column analysis of Fischer-Tropsch products, which occurred in the same oven. Cryogenics were required for the resolution of light hydrocarbons and for the resolution of hydrocarbons from oxygenates in the capillary column. Further details may be found elsewhere (5).

Table I. Analytical Conditions for H₂ Analyses

Sample size	10 µL–1 mL	
Column	1.83 m × 3.18 mm stainless steel packed with 80/100-mesh HayeSep D	
Injection	Source:	Packed-column gas-sampling valve
	Atmospheric balance hold time:	20 s
Zone temperatures	Valve oven:	240°C
	TCD:	130°C (10 µL) and 300°C (1 mL)
	Sample transfer line:	220°C
Column oven temperature program	-10°C (0 min) to 5°C at 2°C/min	
Detector/column information	TCD sensitivity:	high
	Carrier gas:	He
	Analytical column flow rate (30°C):	31 cc/min
	Reference gas flow rate (30°C):	41 cc/min

Results and Discussion

Single-column studies

For analyses using a single 1.83-m HayeSep D column, the effect of detector temperature on TCD signal was determined

initially. For a 250- μ L sample size and a carrier gas flow rate of 24 cc/min (measured at 30°C and ambient pressure), the detector temperature was varied from 150 to 300°C. Figure 2 shows the effect of TCD temperature on the shape of the H₂ peak. The four chromatograms are from Matheson standard gas injections (6% H₂) with TCD temperatures of 150, 200, 250, and 300°C. The nitrogen (N₂) peak was an impurity present in the standard. The 6% H₂ peak changed from positive to negative as the detector temperature increased. Also, the baseline signal decreased with an increase in temperature. These results suggested the use of a low detector temperature for "positive" peak studies (region I of Figure 1A) and a high temperature for "negative" peak studies (region IV of Figure 1B).

Large and small sample sizes corresponding to negative and positive H₂ peaks were explored using the different gas standards. The concentrations in the syngas standards ranged from 32.5 to 66.9% H₂. The Matheson standard contained 6% H₂. For large samples, numerous TCD response curves were generated for H₂ by varying the TCD temperature and sample size (250 and 500 μ L and 1 mL). The HP 3365 Chemstation regression results are shown in Table II. All column flow rates for large sample sizes in Table II were 30 cc/min (measured at 30°C) except for the 250- μ L size at 250 and 300°C (24 cc/min column, 36 cc/min reference). Although the coefficients of determination (r^2) were high, nearly all curves were concave-upward as determined visually from the line plots.

For small sample sizes (10, 20, and 30 μ L), a low TCD temperature (130–140°C) was used to obtain a positive H₂ peak and to maximize the H₂ response. Table II gives the results of the Chemstation regressions. The "positive range" in Table II refers to the range of H₂ concentrations that produced positive Gaussian peak shapes, as determined visually from the chromatograms. For concentrations greater than the upper limit of the positive range, the apex of the peak began to flatten or invert.

Replicates were performed on the two sample sizes (10 μ L and 1 mL) that yielded the widest linear range during the exploratory studies. For each sample size, five replicates of each of the five standards listed previously were analyzed. For the 1-mL sample size, the 10.2% H₂ Scott standard was not used.

For each sample size, the full range of data was initially regressed using an intercept model in MS Excel 5.0 spreadsheet software. The regression results were examined to determine the appropriate linear model. In other words, if the lower and upper 95% confidence intervals

Table II. H₂ TCD Responses for Large and Small Sample Sizes Using a Single Column*

Sample size	Large samples (negative peaks)			Small samples (positive peaks)			
	TCD temperature			TCD temperature: 130–140°C			
	200°C	250°C	300°C	Sample size	Positive range	r^2	
	$(r^2$ values, 6–66.9% H ₂)						
250 μ L		0.971	0.975	0.977	10 μ L	6–66.9%	0.973
500 μ L			0.982	0.980	20 μ L	6–50.3%	0.994
1 mL	0.999			0.990	30 μ L	6–32.5%	1.000

* Exploratory studies with no replicates.

Table III. H₂ Data and ANOVA for Testing Linearity of Regression*

Mole% (x)	Area (y _i)	y _i avg	(y _i - y _i avg) ²		
6.0	268	270.4	6		
6.0	266		19		
6.0	269		2		
6.0	276		31		
6.0	273		7		
10.2	438	440.6	7		
10.2	438		7		
10.2	450		88		
10.2	437		13		
10.2	440		0		
32.5	1404	1422.2	331		
32.5	1472		2480		
32.5	1374		2323		
32.5	1407		231		
32.5	1454		1011		
50.3	1843	1874	961		
50.3	1845		841		
50.3	1993		14161		
50.3	1835		1521		
50.3	1854		400		
66.9	2390	2346.4	1901		
66.9	2386		1568		
66.9	2332		207		
66.9	2328		339		
66.9	2296		2540		
		Pure error sum of squares =	3.10E + 04		
		Error sum of squares =	2.50E + 05		
Error	Sum of squares	Degrees of freedom	Mean square	Computed F	f 0.01
Lack of fit	2.19E + 05	3	7.29E + 04	47.02	4.94
Pure error	3.10E + 04	20	1.55E + 03		

* 10- μ L sample, single column.

for the intercept bracketed the origin, then the data were regressed again in Excel 5.0 using a no-intercept model. The form of the model (intercept versus no-intercept) affects two parameters used in the analysis of variance (ANOVA) test for linearity (6): the residual or error sum of squares (an output of the regression) and the degrees of freedom for the lack-of-fit sum of squares. In the case of the 10- μL and 1-mL sample sizes, the intercept model was appropriate.

The data and the results of the regression were used in an

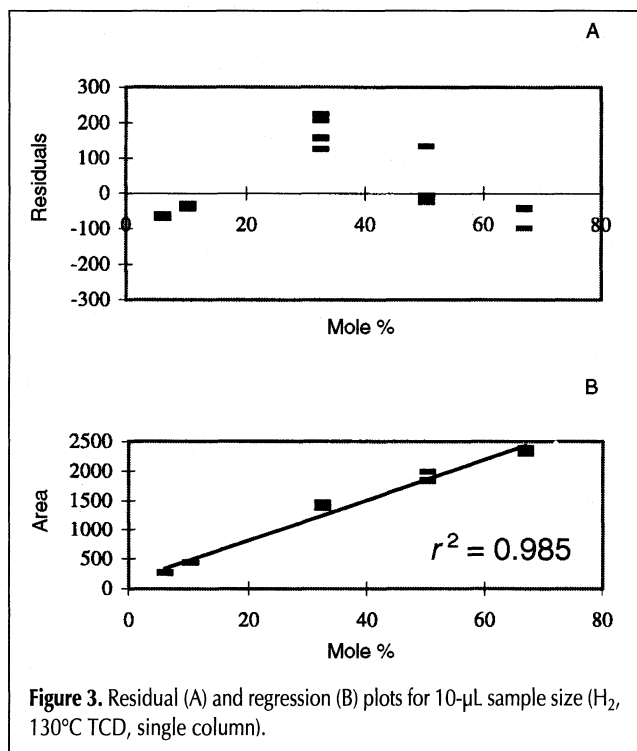


Figure 3. Residual (A) and regression (B) plots for 10- μL sample size (H_2 , 130°C TCD, single column).

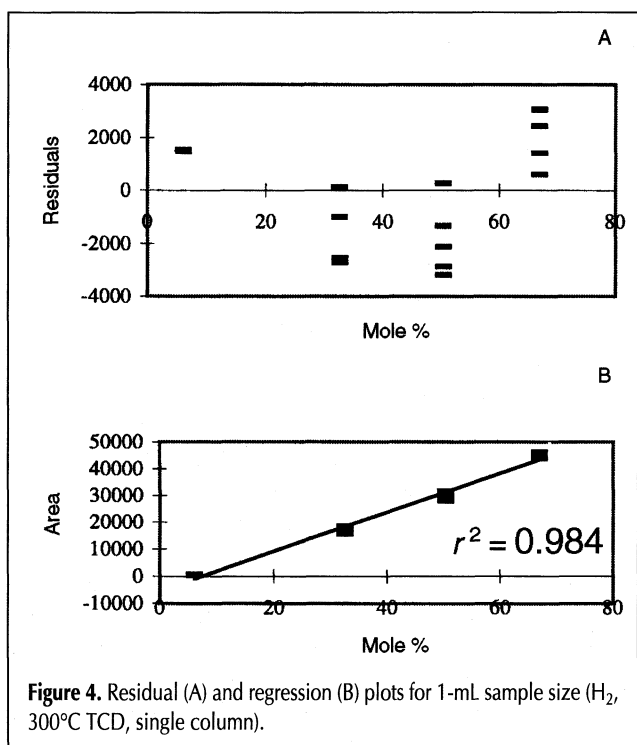


Figure 4. Residual (A) and regression (B) plots for 1-mL sample size (H_2 , 300°C TCD, single column).

ANOVA for testing regression linearity, as outlined in Walpole and Myers (6). When the lack-of-fit component of the error was significant, as it was for the full range of the 10-mL sample data (see Table III, tested at 99% confidence), the linear model was not applicable to the data set, and a subset of data was evaluated. The subset was obtained by deleting all replicates of a concentration located at the ends of the range. The subset was then subjected to the same tests (i.e., model form and linearity). This process was continued until a linear subset of data was found. Such subsets are displayed in Table IV under the column labeled, "Linear range." The residual and line-fit plots over the full range of data are shown in Figures 3 and 4.

Neither parameter set in Table IV produced data that fit a straight line over the entire 6–60% concentration range. The data in Figures 3 and 4 are parabolic. The residuals of the 10- μL sample in Figure 3 exhibit a concave-downward pattern. Although the peaks were positive from 6 to 66.9% (Table II), only the end sections of the curve were linear (6–32.5% and 32.5–66.9% in Table IV). The slope of the high concentration range (32.5–66.9%) was less than that of the low concentration range (6–32.5%). In contrast, the residuals of the 1-mL sample in Figure 4 exhibit an upward concave pattern. Marsman et al. (7), who performed an analysis of products from a fuel methanol reaction, also found that for negative H_2 peaks (275°C TCD, 70- μL sample, 25-m \times 0.53-mm Poraplot Q column), a polynomial provided the best overall fit.

Dual column studies

For analyses using two 1.83-m HayeSep D columns placed in series, the linearity of the low end of the H_2 concentration range was further investigated. The second column was added in order to separate argon (Ar) from carbon monoxide (CO) (required for calculating syngas conversion during Fischer-Tropsch reactions). The added length of column increased the linear range of response; a 30- μL sample produced Gaussian peaks up to 50.3% H_2 (compared with 32.5% H_2 in Table II using a single column). The peaks from two columns in series were not as tall as the peaks from the single column, and this probably contributed to the increase in linearity. Hence a larger sample size (100 μL) was used for the low concentration study. A temperature program of -25°C (0 min) to 5°C at $4^\circ\text{C}/\text{min}$ was used in order to resolve light hydrocarbons in the capillary column. Vacuum calibration (as detailed in reference 1) was used with the Scott 10.2% H_2 -in- N_2 standard to generate a TCD response curve for H_2 . Four replicates were run at six pressures ranging from 61 torr (corresponding to 0.82 mole %) to 736 torr (9.9%).

The resulting data were subjected to the same test for lin-

Table IV. Linearity of H_2 TCD responses from Small- and Large-Sample Replicate Single-Column Studies

Sample size	TCD temperature	Linear range	r^2
10 μL	130°C	6–32.5%	0.998
		32.5–66.9%	0.985
1 mL	300°C	6–50.3%	0.991

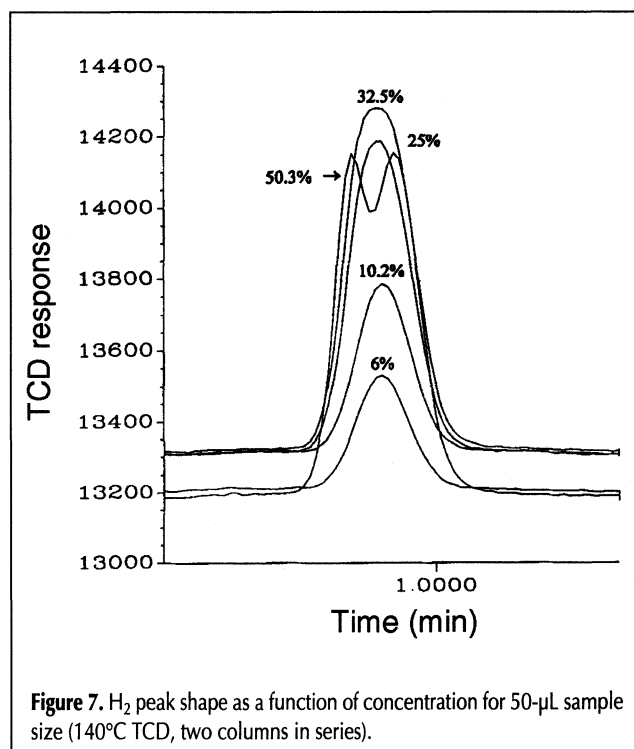
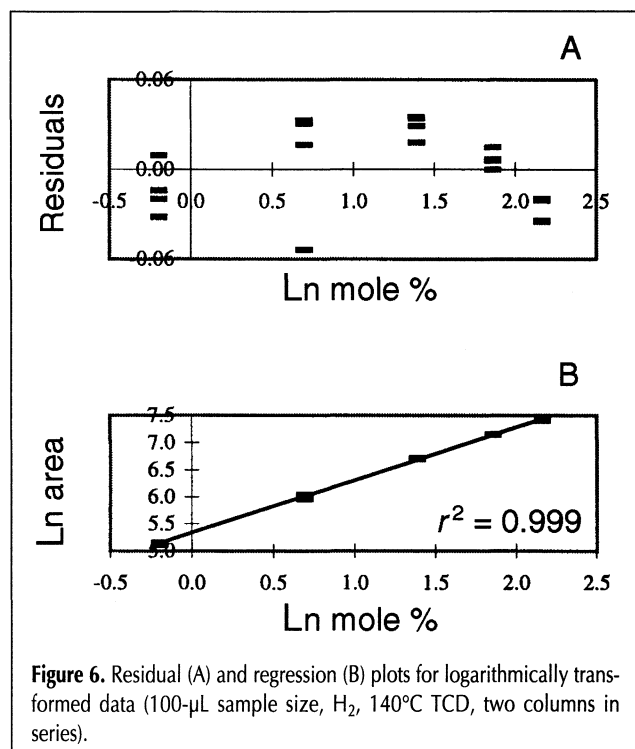
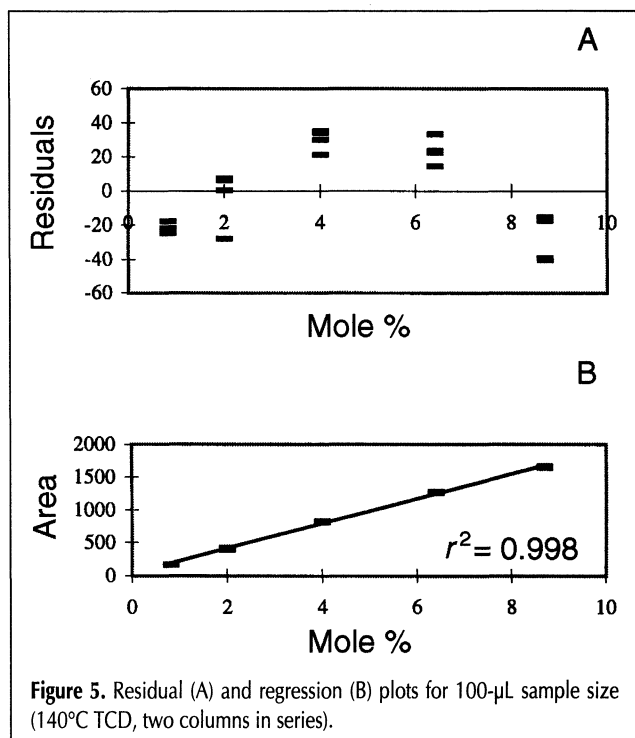
earity that was used with the 10- μ L and 1-mL replicates. From 0.82 to 8.7% H₂, the data were not linear according to the ANOVA test. A logarithmic transformation proved to be more linear (smaller lack-of-fit component), though it failed the linear test as well. Residual and line-fit plots for the original and transformed data are given in Figures 5 and 6.

Villalobos and Nuss (3) reported that a range of H₂ concentrations in region I of Figure 1A produced a linear relationship between peak height and concentration. This region extended

from zero concentration up to a concentration equivalent to roughly half the amount of H₂ required to flatten the apex of the peak (point 3 in Figure 1). The observation of Villalobos and Nuss for TCD response measured in terms of peak height also seems to hold for TCD response measured in terms of peak area. With a single column, the 10- μ L sample size produced a linear area response up to 32.5% H₂ (Table IV) and produced positive peaks up to 66.9% H₂ (Table II).

Villalobos and Nuss also obtained a TCD response curve of relative peak height versus H₂ concentration for a 50- μ L sample size in He carrier gas that was linear to a concentration of roughly 70% (as viewed from the figure in their paper) and suggested this would be a useful, albeit rough, guideline. The TCD and column oven temperatures, sample pressure, carrier gas flow rate, and column were not specified in their paper. Because peak area response curves are more linear than peak height response curves (1,4), one might expect a response curve for peak area to be linear to a concentration beyond 70% H₂ for a 50- μ L sample size. Figure 7 displays the H₂ peaks for a sample size of 50 μ L generated during the current investigation using a flow rate of 30 cc/min (measured at 30°C), 140°C TCD, and no replicates. The series configuration of two HayeSep D columns was used, and the temperature program was -25°C (0 min) to 5°C at 2°C/min. The resulting H₂ peaks were Gaussian up to a concentration of about 25% ($r^2 = 0.999$). The flattening of the peak apex occurred at 32.5% H₂, and peak inversion occurred at 50.3% H₂. In terms of the concentration range of linear response, these results were quite different from those obtained by Villalobos and Nuss for a 50- μ L sample size.

Based on the height response curve of Villalobos and Nuss and the fact that area response is more linear than height response, use of a 10- μ L sample size should produce a linear TCD area response up to 100% H₂ because the amount of H₂



introduced into the He carrier gas stream is less for a 10- μ L sample than for a 50- μ L sample. In other words, the lower concentrations should favor operation in a more linear region, according to Figure 1A. Similarly, use of a 100- μ L sample size should produce a linear TCD area response up to 35% H₂. The TCD responses for the 10- μ L sample obtained using a single column (linear from 6 to 32.5% H₂ in Table IV) and for the 100- μ L sample obtained using two columns in series (nonlinear response for 0.82–8.7% H₂) are also inconsistent with the results of Villalobos and Nuss.

Although it is not possible to make a direct comparison of our results with those of Villalobos and Nuss (due to a lack of knowledge of the analytical conditions they used), it seems plausible that the smaller linear range for H₂ in He carrier gas found during the present study was due to improved resolution in packed columns over the past 30 years. For example, if a given amount of sample is analyzed on two columns of the same length, one of which is a high-resolution column (more theoretical plates per meter) and the other is a low-resolution column, and if all else is the same, the high-resolution column would produce taller peaks. The area of a given peak would be the same on both columns because the amount of sample analyzed is the same, but the peak width would be smaller for the high-resolution column, resulting in a taller peak. In H₂ analysis, the maximum concentration in the Gaussian peak (at the apex) would surpass the linear range of the TCD at a lower mole percentage for a high-resolution column, yielding a concave-downward curve. Hence, the useful guideline set forth by Villalobos and Nuss (i.e., linear TCD response for 0–70% H₂ using a 50- μ L sample) does not appear to be valid with modern-day packed columns.

Conclusion

The TCD response of H₂ using He carrier gas was investigated using HayeSep D packed columns. TCD temperatures were chosen to maximize response, and exploratory studies showed that small and large sample sizes (10 μ L and 1 mL) would potentially yield the widest linear range. However, replicate studies showed that, for the given experimental conditions

and for analyses conducted using a single column, the linear range was rather limited: 6–32.5% H₂ for 10 μ L and 6–50.3% H₂ for 1 mL. In addition, for a 100- μ L sample analyzed on two columns in series, the linear range was even smaller (0.82–8.7% H₂ was nonlinear). The results of the 10- and 100- μ L studies were in sharp contrast to those obtained in an earlier study by Villalobos and Nuss (3), who reported a linear response in the range of 0–70% H₂ using a 50- μ L sample. Improvements in the resolution of packed columns over the last 30 years may help explain the reduced linear range for hydrogen found in the present study.

Acknowledgment

The financial support of the Department of Energy (Grant DE-FG22-92PC92532) is gratefully acknowledged.

References

1. B. Thompson. *Fundamentals of Gas Analysis by Gas Chromatography*. Varian Associates, Palo Alto, CA, 1977, pp. 72–81.
2. C.J. Cowper and A.J. DeRose. *The Analysis of Gases by Chromatography*. Pergamon Press, Oxford, England, 1983, pp. 57–60.
3. R. Villalobos and G.R. Nuss. Measurement of hydrogen in process streams by gas chromatography. *ISA Trans.* **4**: 281–86 (1965).
4. H.M. McNair and E.J. Bonelli. *Basic Gas Chromatography*. Varian Associates, Palo Alto, CA, 1969, p. 151.
5. K. Snaveley and B. Subramaniam. On-line gas chromatography of Fischer-Tropsch products formed in a supercritical reaction medium. *Ind. Eng. Chem. Res.* **36(10)**: 4413–20 (1997).
6. R.E. Walpole and R.H. Myers. *Probability and Statistics for Engineers and Scientists*, 5th ed. Macmillan Publishing Company, New York, NY, 1993, pp. 386–93.
7. J.H. Marsman, B.B. Breman, and A.A.C.M. Beenackers. On-line single column capillary gas chromatographic analysis of all reactants and products in the synthesis of fuel methanol from hydrogen and oxides of carbon. *J. High Res. Chromatogr.* **16**: 141–47 (1993).

Manuscript accepted February 6, 1998.