

Relative Molar Response Factors for Thermal Conductivity Detectors

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Abstract

This paper describes an investigation into the universal nature of relative molar response factors for thermal conductivity detectors. Relative molar response factors are measured on multiple gas chromatographs equipped with thermal conductivity detectors, and the values are compared with values in the literature. As was observed previously, relative molar responses obtained on a single instrument for a homologous series vary linearly with respect to the number of carbon atoms in the hydrocarbon chain. However, significant differences are observed for the slope of this line depending on the instrument studied. This contradicts previous literature results that demonstrated an independence of the relative molar response with regard to the detector. The current results show that the calibration of thermal conductivity detectors using literature values for relative molar response factors could produce significant errors in the concentrations measured by the laboratory chromatograph.

Introduction

Thermal conductivity detectors generally consist of four filaments that are heated with respect to the temperature of the surrounding cavity (1). A reference gas is passed over two of these filaments, and the carrier gas eluting from a gas chromatographic (GC) column is passed over the other two filaments. These four filaments are connected to form a Wheatstone bridge. If the composition of the flow of the column effluent and the reference gas are the same, the heat transfer from each filament to the walls of the cavity is the same, and the Wheatstone bridge is balanced, creating no external voltage. However, when the column effluent contains the carrier gas and another component, there is a change in the rate of heat transfer from the sensing filaments to the cavity walls. This change in heat transfer rate changes the temperature of the filament, which correspondingly changes the resistance to electrical conduction in the filament. Therefore, the Wheatstone bridge becomes unbalanced, creating an external voltage that is proportional to the change in heat transfer and the concentration of the component.

Previous authors have shown that the absolute response of the

thermal conductivity detector to the eluting component cannot be interpreted directly either as a mole percent or as a weight percent (2–4). This is due to the fact that the change in heat transfer is proportional to a number of factors such as flow rate, molar heat capacity, average temperature differences in incoming and outgoing gas, heat loss due to convection, radiation, and end effects (2). This difficulty in data interpretation has been overcome through the use of peak area calibration factors (5–14). The most popular factors are the relative molar response (RMR) factors that were first determined by Rosie and Grob (13). The RMR of a particular compound, i , is defined as follows:

$$\text{RMR}_i = (A_i/A_s) \times (M_s/M_i) \times 100 \quad \text{Eq. 1}$$

where A_i refers to the peak area for component i , A_s refers to the peak area of an internal standard, M_s refers to the mole percent of the internal standard, and M_i refers to the mole percent of component i . Rosie and Grob used benzene as the internal standard and assigned it an arbitrary RMR of 100. The RMR factors were nominally observed to be linear within a homologous series of compounds (2,12). Therefore, within a homologous series, the response of the detector can be interpreted as being proportional to the molar or weight percent of the detected compound in the column effluent. The RMR factors were also found to be independent of a fourfold variation in the flow rate, change in detector temperature from 30 to 160°C, and even the design of the detector or sensing element (12,13).

Because it appeared, according to the literature, that relative response factors were independent of instrumentation, it was thought possible to use this fact in the development of a new method for the validation of natural gas calibration standards. The current method is based on an arbitrary procedure involving the production of a "fidelity" chart for the standard (15). This procedure compares the response factors obtained for the normal paraffins against the molecular weight. The log/log plot of these data appears to be linear, although if the plot is expanded, methane is found to be off the line. If relative response factors were universal, as described in the literature, then an alternative method for standard validation could be developed.

Relative response factors are also important in standard GC in the industrial laboratory. It is common practice to use relative

response factors for a component for which a calibration standard is not readily available or stable. The clearest example is hydrogen sulfide, which is commonly observed to react with cylinder walls and thus decrease in concentration with time. Using a relative response factor for this component allows one to "calibrate" the instrument using a stable component such as ethane.

Experimental

RMR factors for *n*-hexane, *n*-heptane, and *n*-octane were measured using *n*-pentane as an internal standard. In separate solutions, each compound was mixed with an approximately equal mass of *n*-pentane. Each of the alkanes had a purity of at least 99% mol, as determined by GC. The mole percentage of each component in these solutions was calculated based on the mass of each added component and the appropriate molecular weights. Each solution was stored in a crimp-sealed vial until injection. The vials were used promptly in consecutive injections for the tests on each instrument. It is important that the crimp seal vials not be allowed to sit without use after the polymeric septum is pierced with a needle. After a number of days, the *n*-pentane was seen to preferentially evaporate with respect to the other hydrocarbon components of the solutions.

The RMR factors for the normal alkanes from methane to butane were determined using a certified natural gas standard obtained from Phillips Chemical Company (Bartlesville, OK). The gravimetric values supplied by the manufacturer were used as the true values. A plot of the response factors versus the molecular weight was generated to validate the standard prior to use (15).

The chromatograms were obtained on multiple GCs from several manufacturers (Table I). The conditions for each analysis were sufficient to provide baseline separation between each component (Figure 1). The typical GC analysis performed for this

study involved the use of a 30-ft \times $\frac{1}{8}$ -inch-o.d. packed GC column with Silicon DC 200/500 at a 27–30% loading, kept isothermal at 110°C. The column flow rate was set at 35 mL/min, and the detector was heated to 150°C.

The natural gas samples were injected into the GCs using a 0.25-mL gas sample loop. The binary liquid mixtures of pentane with hexane, heptane, or octane were syringe injected into the GCs using a 10- μ L syringe.

The RMR factors for each GC were determined after ensuring the repeatability and linearity of each of the GC analyses. The RMR factors were calculated following the procedure used by Rosie and Grob (13) with the exception that pentane was used as the reference rather than benzene. Whenever possible, the RMR factors were based on triplicate analyses. The RMR factors of the normal alkanes from methane to octane are shown in Table II for each GC. Each instrument is designated numerically. The instruments designated as "2a" and "2b" are separate instruments of the same model and manufacturer. The most recent literature RMR values for the alkanes (14) were recalculated using *n*-pentane as the internal standard and are also shown in Table II.

Results and Discussion

From the data, the relative response factors for each separate GC were observed to be linear with respect to the length of the hydrocarbon chain. This observation is consistent with the results originally obtained by Rosie and Grob (13) and is supported by the fact that plots of the RMR factors versus molecular weight are generally linear (Figure 2) with correlation coefficients around 0.99 (Table II). However, there are significant slope differences between the RMRs determined on the various instruments. In fact, the slope varies from 0.92 to 1.23, which results in a difference of nearly 50% in the methane RMR factor.

It should be noted that the plot of RMR versus molecular weight is not expected to be exactly linear. The original investigations indicated that the RMR of the first members (lowest carbon number) of the homologous series would fall off a plot of RMR versus molecular weight (2,6,12). To test this, the linear least square fit of the data was used to predict an RMR for methane for all the data. These results were compared with the experimental values (Figure 3). The first bar for each instrument is the RMR obtained experimentally, the second bar is the predicted RMR value for methane, and the third bar is the difference between the experimental and the predicted value. The data from Dietz (14) shows that the experimental value is larger than the predicted value, as is true for the data obtained for GCs 2a and 2b, which are the same model of GC. All other instruments showed an RMR for methane lower in value in comparison with the predicted values.

The cause of the deviation of the lower carbon number homologues from the linear correlation between RMR and molecular weight was not determined in the original publications. It was noted that the plot of molecular weight versus RMRs obtained for a homologous series using

Manufacturer and model	Instrument
Hewlett-Packard 5790	dual filament TCD
Hewlett-Packard 5880	single filament TCD
Hewlett-Packard 5890	single filament TCD
Hewlett-Packard 6890	single filament TCD
Carle	dual thermistor TCD
Trimetrics	dual filament TCD

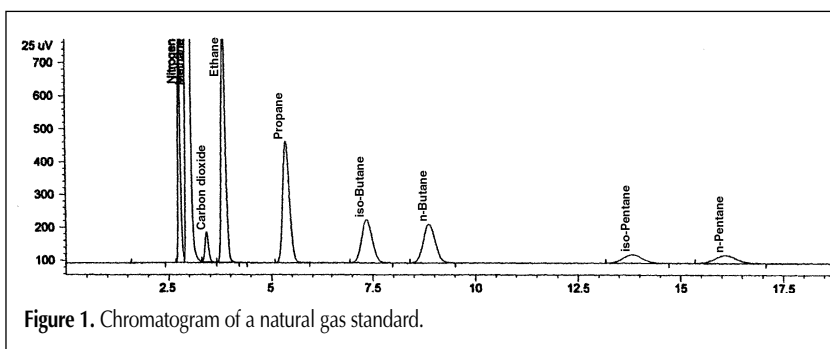
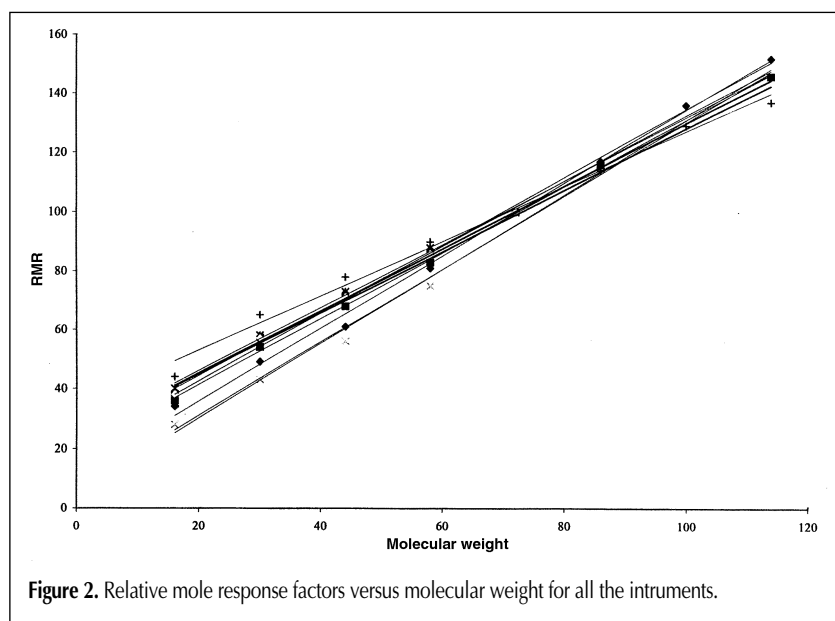
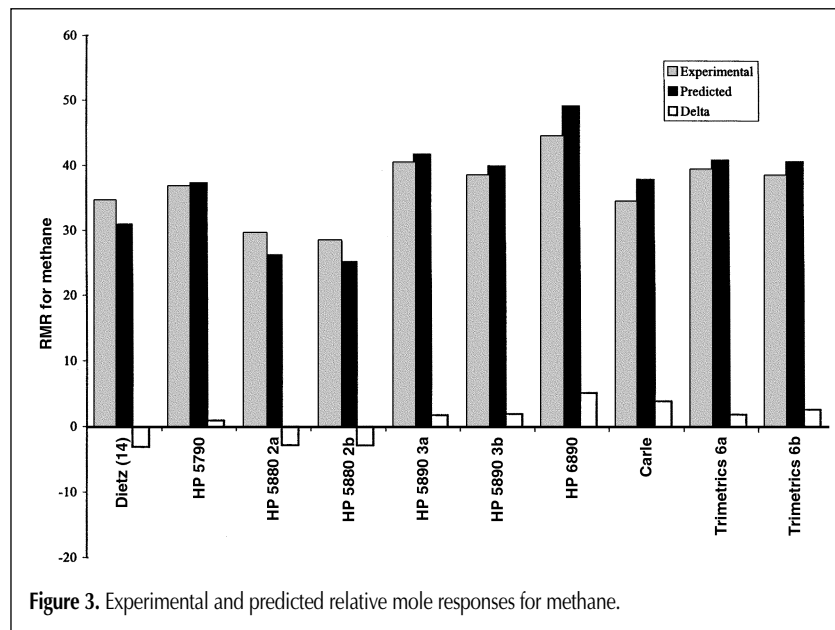


Figure 1. Chromatogram of a natural gas standard.

Table II. RMR Factors for Normal Alkanes

	C ₁	C ₂	C ₃	n-C ₄	n-C ₅	n-C ₆	n-C ₇	n-C ₈	Slope*	r ² *
Dietz [†]	34	49	61	81	100	117	136	152	1.23	0.9972
GC 1	36	54	68	83	100	116	146		1.12	0.9994
GC 2a	29	44	56	75	100				1.23	0.9797
GC 2b	28	43	56	75	100				1.25	0.9824
GC 3a	40	58	73	88	100				1.07	0.9952
GC 3b	38	57	72	87	100				1.10	0.9953
GC 4	44	65	78	90	100	114	129	137	0.92	0.9915
GC 5	34	58	72	87	100				1.15	0.9845
GC 6a	39	57	72	86	100	114			1.06	0.9977
GC 6b	38	57	71	86	100	111			1.04	0.9942

* Slope and correlation coefficient r^2 calculated from RMR versus molecular weight.[†] Reference 14.**Figure 2.** Relative mole response factors versus molecular weight for all the instruments.**Figure 3.** Experimental and predicted relative mole responses for methane.

nitrogen as a carrier showed a strong deviation from linearity. It was suggested that this deviation is related to the fact that thermal conductivity is a decreasing function of molecular weight, and for the higher homologues, the differences in the thermal conductivity approached a limiting value.

The variation in the slope of the plots of RMR versus molecular weight clearly demonstrates that the RMR values are not independent of the instrument being used. Furthermore, given that the conditions on all the instruments were nearly identical and well within the conditions tested in the literature, it becomes evident that the assertion by Messner et al. (12) that the relative response factors are independent of filament and detector design appears to be incorrect.

The differences in the RMRs for each instrument can easily be represented by taking the ratio of the RMRs obtained for each compound and dividing them by the RMRs reported in the literature (Table III). These data demonstrate that the RMRs obtained differ between -19% to +29% from the RMRs originally reported by Dietz (14). These differences, coupled with the good correlation of the RMRs with molecular weight, clearly demonstrate the dependence of RMR on the instrument.

Further analysis of the RMRs found in Tables II and III reveals that the RMR factors are representative of a specific model of thermal conductivity detector. There were three sets of data obtained using two independent instruments of the same design. The data obtained for one GC (2a) was similar to the data obtained on a second GC of the same design (2b). This observation is also true of the data obtained from GC 3a and 3b and GC 6a and 6b. All three sets of instruments show self-consistent data. This is probably a trend that can be seen for all GC designs.

In an attempt to determine the cause of the discrepancy between the data obtained in our labs and that originally obtained by Messner (12), the RMRs were determined at effluent flow rates between 5 and 50 mL/min (Table IV). Surprisingly, these data show a 15% change in the RMR factor for methane. The RMR factors of methane, ethane, propane, and *n*-butane all decreased as the flow rate of the carrier decreased, although the effect was attenuated for the higher homologues.

Messner suggested that the RMR factors were independent of flow rate over a fourfold range (12). However, Messner's measurements of the propane RMRs were performed with flow rates between 33 and 120 mL/min. In this range, our data and Messner's data indicates that the RMR factors are invariant to flow rate. Our flow rate of 34.3 mL/min corresponds well with the lowest flow rate used in Messner's study. Unfortunately, the instrument used in our flow rate study was unable to maintain a flow rate greater than 60 mL/min.

Next, there was an attempt to confirm the independence of the RMR factors on the temperature

Table III. Ratio of Observed Versus Literature Values*

	C ₁	C ₂	C ₃	n-C ₄	n-C ₅	n-C ₆	n-C ₇	n-C ₈
GC 1	1.06	1.11	1.10	1.02	1.00	0.99		0.96
GC 2a	0.84	0.90	0.91	0.93	1.00			
GC 2b	0.81	0.88	0.91	0.93	1.00			
GC 3a	1.18	1.19	1.19	1.08	1.00			
GC 3b	1.12	1.17	1.18	1.07	1.00			
GC 4	1.29	1.33	1.27	1.12	1.00	0.98	0.95	0.90
GC 5	1.01	1.19	1.18	1.07	1.00			
GC 6a	1.15	1.17	1.18	1.06	1.00	0.98		
GC 6b	1.12	1.17	1.16	1.06	1.00	0.95		

* Literature values obtained from Dietz (14).

Table IV. Variation of RMR with Respect to Flow Rate

Flow rate (mL/min)	Methane	Ethane	Propane	n-Butane
5	38.2	59.6	74.6	88.6
10	39.2	61.0	75.7	89.0
20	41.9	63.5	77.4	89.9
34.3	44.0	65.0	78.0	90.0
50	45.0	65.1	78.2	90.0

Table V. Variation of RMR Factors with Respect to Temperature

Temperature differential (°C)	Methane	Ethane	Propane	n-Butane
165	44	65	78	90
140	43	64	77	89
120	42	63	77	89

difference between the filament and the block of the thermal conductivity detector. The temperature of the thermal conductivity detector for GC was varied between 120 and 165°C, and the RMRs were determined (Table V). The data suggests that there is possibly a slight downward trend of the RMR factors as the temperature differential between the filament and the cavity wall decreases.

Conclusion

RMR factors are portable between detectors of the same design. However, the RMR factors determined for one detector design are not portable to another type of thermal conductivity detector. These results contradict current accepted practices that RMR factors are universal. Under low column flow rate conditions (< 35 mL/min), RMR factors obtained on a single detector can

vary with the flow rate.

The results from these studies indicate that further investigation into the variation of RMR factors between different instruments is advisable. Possibly, the advent of more sensitive detectors and more efficient columns, which has resulted in lower flow rates, allows some flow-rate-dependent mechanism to contribute to the RMRs. This mechanism could be inherent in the design of the thermal conductivity detector; perhaps it is a slower heat transfer to the detector body at lower flow rates. Whether this mechanism creates the observed discrepancy in the RMRs or some other mechanism is responsible, relative response factors should be used with caution.

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