



ELSEVIER

Journal of Chromatography A, 841 (1999) 187–195

JOURNAL OF
CHROMATOGRAPHY A

Thermal conductivity detection relative molar response factors for halogenated compounds

M.J. Height, E.M. Kennedy*, B.Z. Dlugogorski

Industrial Safety and Environment Protection Group, Department of Chemical Engineering, The University of Newcastle, Callaghan NSW 2308, Australia

Received 29 October 1998; received in revised form 4 March 1999; accepted 10 March 1999

Abstract

Relative molar response (RMR) factors for the thermal conductivity detector have been determined for a number of halogenated compounds. The compounds investigated included seven gases, namely CHF_3 , CBrF_3 , CH_3Cl , CHClF_2 , C_2HClF_4 , C_3F_8 and C_4F_{10} , and seven liquids, 2,3-dichloro-1-propene, 1-chloro-2-methyl-1-propene, 1,1,1-trichloroethane, *m*-dichlorobenzene, 1-bromo-3-chloropropane, 1-bromo-3-chloro-2-methylpropane and 2-bromopropane. Experimentally determined RMR values for these compounds were compared to theoretical predictions to examine the suitability of a predictive technique for halogenated compounds. Good agreement with predicted values has been found between both experimental and literature data, indicating that the predictive technique is applicable for halogenated species. The accuracy of the predictive technique is excellent for low-molecular-mass halogenated compounds, with the accuracy decreasing for molecules with more carbon atoms, molecules with iodine atoms and unsaturated halocarbons. An analysis of the relative errors associated with gas chromatographic quantification using assumed and predicted RMR factors was also undertaken. The predictive technique was found to provide a good estimation of RMR factors for compounds with limited response data. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Thermal conductivity detection; Detection, GC; Relative molar response factors; Halogenated compounds

1. Introduction

Thermal conductivity detection (TCD) is one of the simplest and most widely utilised detection methods in gas chromatography (GC). The response (signal strength) of TCD to various solutes, quantified in terms of relative molar response (RMR) factors, has been reported in literature, for example, in a widely referenced article [1]. RMR factors correct for differences in detector response to differ-

ent compounds, giving more representative and reliable quantification.

A theoretical technique to predict RMR factors based on critical thermodynamic properties of compounds is reported in Ref. [2]. The prediction technique is particularly useful for quantification of more obscure chemical species that may be identified using a GC–MS and potentially quantified by TCD. Calculation of relative response from critical thermodynamic parameters is often a more practical alternative to conventional sample calibration techniques for these obscure compounds.

Halogenated compounds are used extensively for

*Corresponding author.

refrigeration and fire suppression duties. Gas chromatographic quantification of halogenated compounds in fire suppression studies requires knowledge of RMR factors. RMR values for halogenated compounds are not widely reported in literature and this study aimed to determine if this predictive technique can be applied to halogenated species.

2. Theory

2.1. Application of RMR factors

The TCD response to various compounds is reported on a relative scale with benzene arbitrarily assigned a value of 100. RMR factors are best suited to finding the mole percent of components in a sample. Dividing chromatogram peak areas by the RMR value of the corresponding compound gives the true response [1]. Normalising the true response values provides the mole percent of each component. The use of RMR factors compensates for compound-dependent detector response, and allows determination of the molar composition of a given sample. RMR factors are independent of filament type, temperature, carrier flowrate and solute concentration [4]. The accuracy of these values is reported to be $\pm 3\%$ [1].

2.2. RMR prediction

The prediction technique developed in Ref. [2] is derived from kinetic theory. The predicted response of compounds in various carrier gases is given by Eq. (1).

$$\text{RMR}_i = \left[\frac{\sigma_i + \sigma_1}{\sigma_\phi + \sigma_1} \right]^2 \left[\frac{M_i - M_1}{M_\phi - M_1} \right]^\alpha \cdot 100 \quad (1)$$

where σ signifies the collision diameter (\AA), M the molecular mass and the subscripts i , 1 and ϕ refer to the solute under consideration, the carrier gas and a standard species (benzene). The superscript α is equal to 0.25 for light carrier gases (helium or hydrogen) and 0.50 for heavy carrier gases (nitrogen or argon) [3]. The factor of 100 represents the arbitrary response of benzene as an internal standard. The collision diameter (σ) may be found from

Table 1
Expressions for estimating collision diameter

Eq.	Collision diameter expression (\AA)	Original source
(2)	$\sigma = 0.618V_c^{1/3}T_c^{1/18}$	[5]
(3)	$\sigma = 0.561V_c^{5/12}$	[5]
(4)	$\sigma = (0.8123 + 0.1678\omega)V_c^{1/3}$	[6]
(5)	$\sigma = 110.2423(T_c/P_c)^{1/3}$	[6]

reported data or from empirical correlations. Nine expressions for σ were considered in the study reported in Ref. [2] and the expressions found to be most suitable for the species in the present study are given by Eqs. (2)–(5), as shown in Table 1.

In Table 1, T_c denotes critical temperature (K), V_c stands for critical volume (cm^3/mol), P_c signifies critical pressure (Pa) and ω indicates the acentric factor. These critical parameters are widely reported in thermodynamic tables for numerous species [7,8]. The critical parameters for the compounds considered in this study are listed in Table 2. A variety of correlations are available for estimating critical properties of uncommon species with incomplete or sparsely reported thermodynamic properties [9]. Expressions for estimating the acentric factor are reported in [7].

3. Experimental

A Shimadzu GC-17A gas chromatograph equipped with a Shimadzu TCD-17 thermal conductivity detector was used in this study. For all experiments, the TCD system was maintained at 200°C with a filament current of 50 mA. The output signal from the gas chromatograph was processed with a 21-bit A/D unit and analysed with peak integration software on a Macintosh computer (SMADchrom).

A J&W Scientific GS-Q capillary column (30 m \times 0.32 mm) was used isothermally at a temperature of 100°C for the analysis of gaseous compounds. An externally mounted six-port gas sampling valve (Valco) with a 100-mm³ loop was used for on-line sample injection of the gases. Helium (BOC Gases, 99.999% purity) was used as the carrier gas with a flowrate of 2.0 cm^3/min and split ratio of 60:1. Nitrogen (BOC Gases, 99.999% purity), acting as the internal standard, was passed through the sample

Table 2
Critical thermodynamic parameters for halogenated compounds studied

Compound	Formula	T_c (K)	P_c (kPa)	V_c (cm ³ /gmol)	ω	Source
Trifluoromethane (FE-13)	CHF ₃	299.30	4860	132.70	0.260	[7]
Methylchloride	CH ₃ Cl	416.30	6700	138.90	0.153	[7]
Chlorodifluoromethane (HCFC-22)	CHClF ₂	369.30	4970	165.60	0.221	[7]
Bromotrifluoromethane (Halon 1301)	CBrF ₃	340.15	3972	200.00	0.173	[8]
Chlorotetrafluoroethane (HCFC-124)	C ₂ HClF ₄	395.70	3630	242.48	0.286	[10]
Octafluoropropane (FC-2-1-8)	C ₃ F ₈	345.05	2680	299.00	0.326	[8]
Decafluorobutane (FC-3-1-10)	C ₄ F ₁₀	386.35	2323	397.00	0.372	[8]
2,3-Dichloro-1-propene	C ₃ H ₄ Cl ₂	577.00	4380	277.00	0.206	[8]
1-Chloro-2-methyl-1-propene	C ₄ H ₇ Cl	537.50	4022	286.34	0.186	[9]
1,1,1-Trichloroethane	C ₂ H ₃ Cl ₃	545.00	4296	281.00	0.216	[8]
<i>m</i> -Dichlorobenzene	C ₆ H ₄ Cl ₂	683.95	4070	351.00	0.279	[9]
1-Bromo-3-chloropropane	C ₃ H ₆ BrCl	644.30	4706	309.49	0.299	[9]
1-Bromo-3-chloro-2-methylpropane	C ₄ H ₉ BrCl	416.30	4153	362.26	0.313	[9]
2-Bromopropane	C ₃ H ₇ Br	532.00	5510	266.00	0.243	[8]

loop at a flowrate of 100 cm³/min, at a pressure of 138 kPa and a temperature of 18°C. Nitrogen samples were injected using the valve and a chromatograph peak area corresponding to pure nitrogen was obtained. Halogenated compounds (generally >99% purity) were passed through the sample loop at the same flowrate, pressure and temperature as for the nitrogen, and injected into the GC system in an identical manner. The resulting chromatogram peak areas for the halogenated compounds were then compared to the nitrogen standard to determine the RMR of each species. The following equation was used to determine the RMR values from the chromatogram areas,

$$\text{RMR}_i = 42 \left(\frac{A_i}{A_{N_2}} \right) \quad (6)$$

where RMR_{*i*} indicates the unknown response factor, A_{*i*} and A_{N₂} are the unknown and standard (nitrogen) species chromatogram areas. The gaseous compounds considered in the experiments were CH₃Cl, CHF₃ (FE-13), CHClF₂ (HCFC-22), CBrF₃ (Halon 1301) C₂HClF₄ (HCFC-124), C₃F₈ (FC-2-1-8) and C₄F₁₀ (FC-3-1-10). The factor of 42 used in Eq. (6) is the relative molar response of nitrogen with respect to benzene.

A J&W Scientific DB-5 capillary column (25 m × 0.25 mm) was utilised for the analysis of the liquid compounds. An isothermal column temperature of 80°C, a helium carrier gas flowrate of 1.0 cm³/min

and a split ratio of 100:1 were used for all experiments. As for the gaseous sample experiments, the TCD system was operated at 200°C and a filament current of 50 mA. Measured quantities of each halogenated compound and benzene were mixed together (gravimetrically), producing mixtures of known mol% composition in an identical manner to the experiments of Ref. [2]. The mole fraction of halogenated compound in benzene was typically 10% and the injected liquid sample size was maintained at 0.2 mm³. The resultant chromatogram for each binary mixture was then used in conjunction with Eq. 7 to determine the RMR of the halogenated species,

$$\text{RMR}_i = 100 \left(\frac{A_i}{A_B} \right) \left(\frac{1-n}{n} \right) \quad (7)$$

where RMR_{*i*} is the unknown response factor, A_{*i*} and A_B are the halogenated and standard (benzene) species chromatogram areas and *n* is the known mole fraction of halogenated species in the injected sample. The liquid compounds considered in this study were 2,3-dichloro-1-propene, 1-chloro-2-methyl-1-propene, 1,1,1-trichloroethane, *m*-dichlorobenzene, 1-bromo-3-chloropropane, 1-bromo-3-chloro-2-methylpropane and 2-bromopropane.

4. Results and discussion

The relative molar response values found from

Table 3
Experimental and predicted RMR factors for halogenated species with helium carrier gas (benzene = 100)

Compound	State (25°C)	Experimental RMR	Predicted RMR	Error ^a (%)	Equation for σ
Trifluoromethane (FE-13)	Gas	64.2	69.5	-8.3	(2)
Methylchloride	Gas	68.5	66.3	3.2	(2)
Chlorodifluoromethane (HCFC-22)	Gas	84.6	81.8	3.3	(2)
Bromotrifluoromethane (Halon 1301)	Gas	120.2	101.5	15.6	(2)
Chlorotetrafluoroethane (HCFC-124)	Gas	103.6	109.5	-5.7	(2)
Octafluoropropane (FC-2-1-8)	Gas	140.4	129.2	8.0	(4)
Decafluorobutane (FC-3-1-10)	Gas	194.4	157.9	18.8	(3)
2,3-Dichloro-1-propene	Liquid	126.7	113.7	10.3	(3)
1-Chloro-2-methyl-1-propene	Liquid	86.1	109.8	-27.5	(3)
1,1,1-Trichloroethane	Liquid	109.5	120.2	-9.8	(3)
<i>m</i> -Dichlorobenzene	Liquid	135.5	139.6	-3.0	(3)
1-Bromo-3-chloropropane	Liquid	134.3	132.3	1.5	(3)
1-Bromo-3-chloro-2-methylpropane	Liquid	152.5	148.0	3.0	(3)
2-Bromopropane	Liquid	124.5	114.8	7.8	(4)

^a Where Error(%) = $100 \times (\text{experimental RMR} - \text{predicted RMR}) / \text{experimental RMR}$.

experiments for the halogenated compounds are compared to the corresponding theoretical predictions in Table 3. Further comparison of the experimental and predicted RMR values is illustrated in Fig. 1.

For the gaseous compounds studied, the predicted RMR values for CH₃Cl, CHClF₂, C₂HClF₄ and C₃F₈ are very close (within 3.5%) to the corresponding experimental values. Close correlation between prediction and experiment was also observed for CHF₃, with the agreement between the predicted and experimental values being within the associated error margins. A less successful level of agreement is observed for CBrF₃ and C₄F₁₀ compounds. This may be attributed to limitations in the experimental technique and the lower purity of these samples due to the presence of nitrogen. Additional error may derive from Eq. (2) giving less exact prediction for the larger C₄F₁₀ molecule.

The predicted response factors for the liquid compounds corresponded favourably with the experimental values. The predicted and experimental RMR values for *m*-dichlorobenzene, 1-bromo-3-chloropropane and 1-bromo-3-chloro-2-methylpropane were each in agreement to within 3%. The excellent agreement between the experimental and literature values for 2-bromopropane suggests that the experimental technique and analysis are satisfactory. A lower degree of agreement was observed for

1,1,1-trichloroethane and 2-bromopropane, with the prediction falling within 10% of the experimental values, yet still within the anticipated error range of experiment and prediction. Less accurate correlation was observed for 2,3-dichloro-1-propene and 1-chloro-2-methyl-1-propene, indicating a potential deficiency in the prediction correlation for unsaturated species. A comparison between predicted and literature response factors [11] is given in Table 4.

The influence of detector temperature, filament current, carrier flowrate and solute concentration were also examined. The measured response factors were found to be independent of detector temperature and current, as reported in Ref. [4], and also independent of carrier settings sufficient to ensure detector overload is avoided (high split ratios and high carrier flowrates).

Based on the compounds considered in this study, the predictive technique developed by Barry and Rosie [2] is suitable for providing accurate estimates of the RMR for lighter (C₁, C₂, C₃) halogenated species and may be extended, with caution, to higher molecular mass compounds. The comparison between predictions and the experimentally determined values of Ref. [11] yields additional insight into the applicability of this method. The use of nitrogen as the internal standard for the present study, and benzene and toluene in Ref. [11], also gives a breadth of experimental values for comparison with

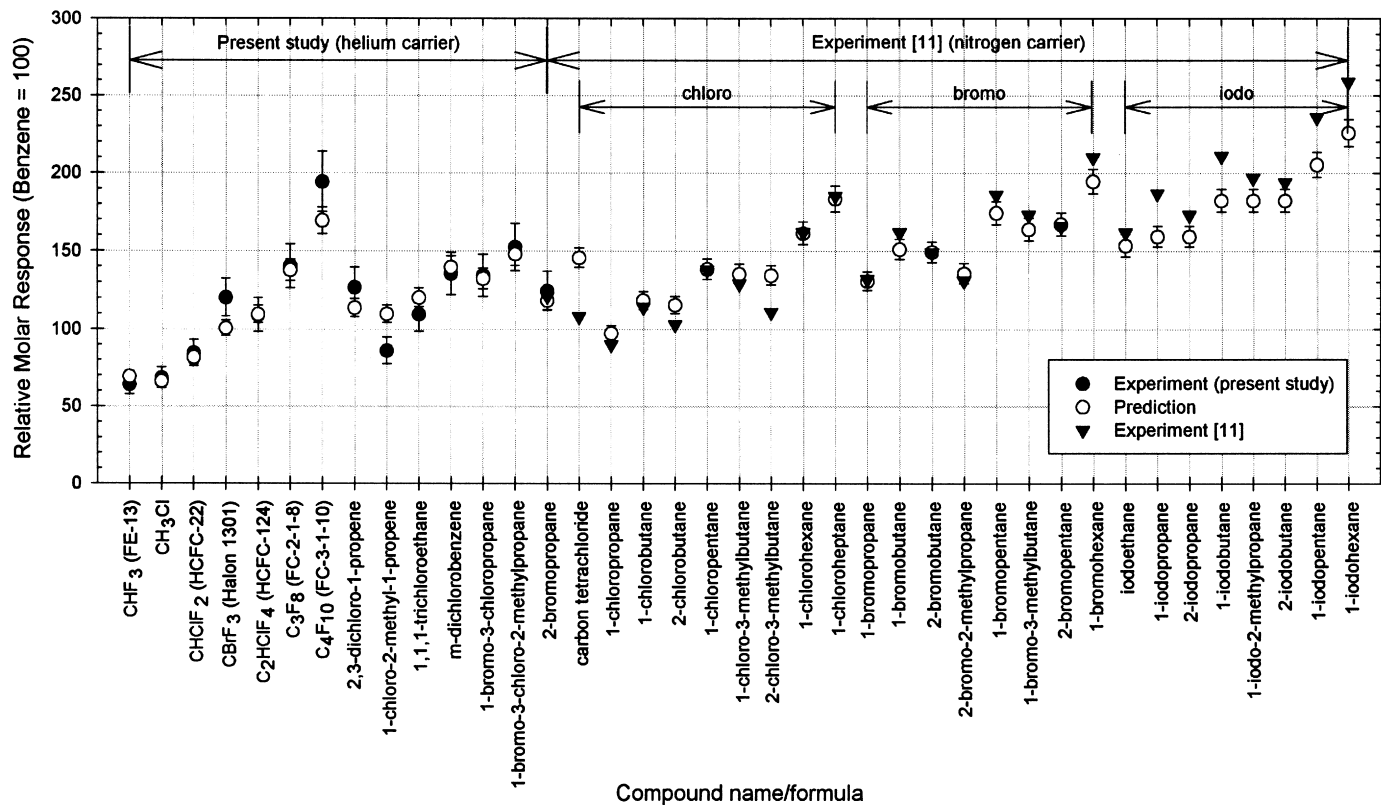


Fig. 1. Comparison of experimental and predicted RMR factors.

Table 4
 Experimental [11] and predicted RMR factors with nitrogen carrier gas (benzene = 100)

Compound	Experimental RMR [11]	Predicted RMR	Error ^a (%)
2-Bromopropane	121	118.3	2.2
Carbon tetrachloride	108	145.6	-34.8
1-Chloropropane	90	97.3	-8.1
1-Chlorobutane	114	118.4	-3.9
2-Chlorobutane	103	115.5	-12.1
1-Chloropentane	138	138.3	-0.2
1-Chloro-3-methylbutane	129	135.2	-4.8
2-Chloro-3-methylbutane	111	134.4	-21.1
1-Chlorohexane	162	161.4	0.4
1-Chloroheptane	185	183.4	0.9
1-Bromopropane	132	130.7	1.0
1-Bromobutane	162	151.2	6.7
2-Bromobutane	149	149.3	-0.2
2-Bromo-2-methylpropane	131	135.6	-3.5
1-Bromopentane	186	174.4	6.2
1-Bromo-3-methylbutane	173	163.9	5.3
2-Bromopentane	166	167.1	-0.7
1-Bromohexane	210	194.7	7.3
Iodoethane	162	153.5	5.2
1-Iodopropane	187	159.3	14.8
2-Iodopropane	173	159.3	7.9
1-Iodobutane	211	182.3	13.6
1-Iodo-2-methylpropane	197	182.3	7.5
2-Iodobutane	194	182.3	6.0
1-Iodopentane	236	205.4	13.0
1-Iodohexane	259	225.9	12.8

^a Where Error% = $100 \times (\text{experimental RMR} - \text{predicted RMR}) / \text{experimental RMR}$.

prediction. Similarly, the use of two different carrier gases, helium in the present experiments and nitrogen in Ref. [11], allows the accuracy of the prediction method to be thoroughly tested. The prediction compares very well with the data for chlorinated and brominated species, but discloses shortcomings for iodinated compounds. The accuracy of the prediction may also be seen to decrease as the number of carbon atoms increases. The trend of lower predictive accuracy from chloro to iodo and from C₁ to C₆ species suggests that the relative response is a stronger function of molecular size than is presently accounted for by the model. There is no observed decrease in accuracy for compounds with mixed halogenated atoms (e.g. CHClF₂, C₂HClF₄ and 1-bromo-3-chloro-2-methylpropane), reinforcing the suitability of this technique to aid with the quantification of refrigerant and fire suppression compounds. The predictive technique may therefore be used with

confidence for C₁–C₃ halogenated species, and be extended to larger compounds with an awareness of errors arising from the presence of iodine atoms, unsaturated haloalkanes and increasing molecular size. The predictive technique has also been used to find the RMR factors for an additional series of halogenated compounds (Table 5). These values are yet to be confirmed experimentally.

4.1. Significance of RMR factors

In many instances, if the response factor of a compound is not known, it is convenient to adopt the response factor value of a compound with similar structural and physical properties to the compound being analysed. This approach often works well for compounds of very similar structure and physical properties. However, a large degree of error can be introduced into the analysis if the assumption of

Table 5
Predicted RMR factors for various halogenated compounds in helium carrier gas

Compound	Predicted RMR
CF ₄	73.9
CClF ₃	87.8
CCl ₂ F ₂	100.6
CCl ₃ F	112.1
CHClF ₂	81.8
CHCl ₂ F	93.5
CHCl ₃	107.4
CBrClF ₂	116.2
CF ₃ I	116.0
C ₂ H ₄ F ₂ (HFC-152a)	79.4
C ₃ HF ₇ (HFC-227ea)	125.9
C ₆ F ₁₄	222.9
3-Bromotoluene	151.6
2-Monochloronaphthalene	65.9
2-Bromonaphthalene	78.6
HCl	47.9
HF	38.6

similarity is inappropriate. The percentage error in the measured composition of a binary mixture arising from the assumption of an incorrect response factor is given by Eq. (8).

$$\text{Error}(\%) = \frac{|1 - (R_{1A}/R_{1T})| \times 100}{1 + (R_{1A}/R_{1T})((1/\phi) + \phi)} \quad (8)$$

where $\phi = (A_2/A_1)(R_{1A}/R_2)$, R_{1A} and R_{1T} are the assumed and true response factors for species 1, R_2 is the true (known) response factor for species 2 in the binary mixture and A_1 and A_2 are the chromatogram peak areas for species 1 and 2, respectively. The maximum composition error for various ratios of assumed and true response factor are plotted (Fig. 2) along with the value of ϕ giving the maximum error.

An immediate observation from Fig. 2 is that, if the response ratio (ratio of assumed RMR to true RMR) is unity, then there will be no error in the

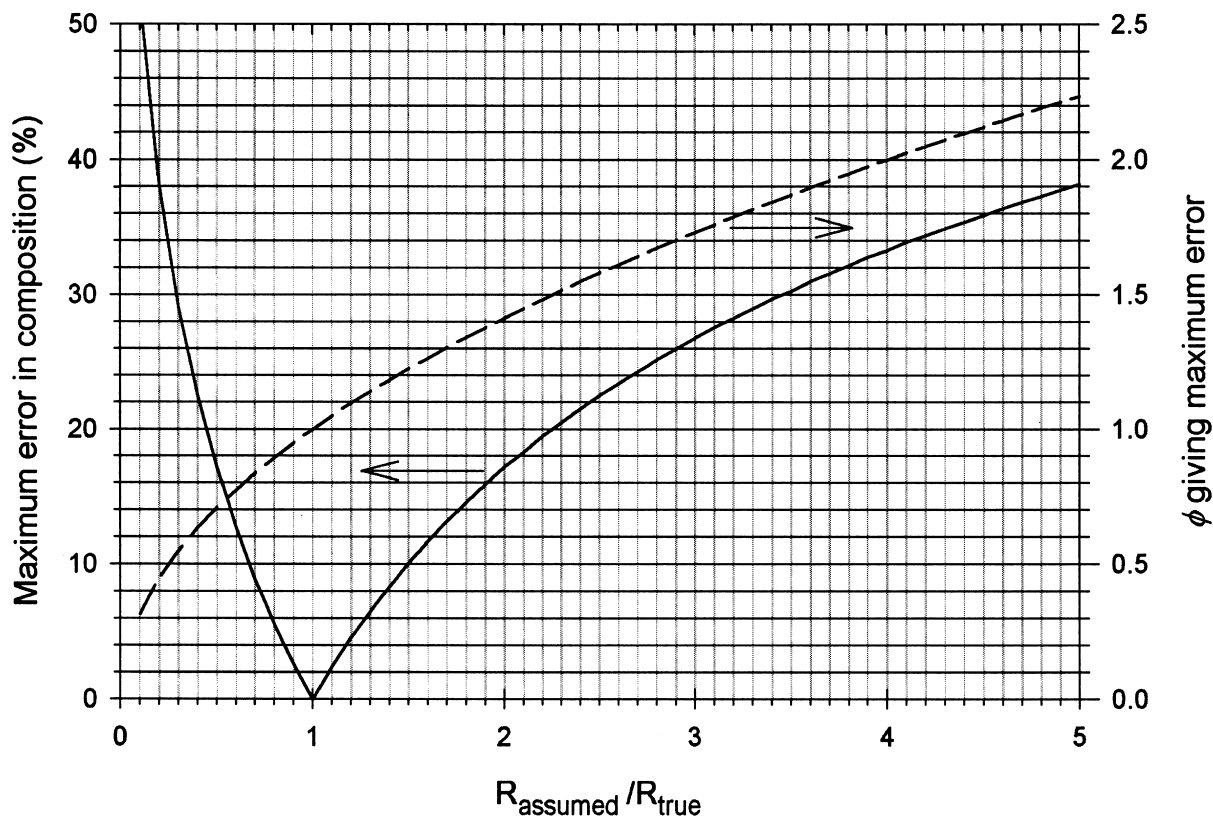


Fig. 2. Plot showing the maximum error in binary mixture composition arising from assuming an incorrect RMR factor for one species.

calculated composition. Therefore, if the response of a very similar compound is chosen, then it is likely that any resulting composition errors will be small. However, the errors in composition increase sharply as the response ratio moves away from unity. By assuming a response factor value of a compound that is dissimilar to the actual species, this can therefore potentially lead to significant composition errors. The use of maximum error in composition in this context serves as an upper limit to errors arising from the choice of response factor. The ratio of chromatograph peak areas giving rise to the maximum error is dependent on the second species in the binary mixture and can be determined by using ϕ from Fig. 2 and the definition of ϕ in Eq. (8).

For common compounds, if a response factor is not known there are often data available for many compounds that are similar to the principal species, and there would be little advantage in using a predictive approach. The strength of the predictive technique [2] is that it can often provide a closer estimate to the true compound response factor than may be possible from adopting the response of a dissimilar compound.

There is minimal response factor data available for halogenated compounds, and experimental determination of response factors can be expensive, dangerous and time-consuming, particularly for uncommon species. The predictive approach is therefore an appealing alternative to assuming responses from a limited selection of data. For example, consider a binary mixture with 2-bromopropane. If the assumed response was taken as the predicted value 114.8 (Table 3) and the true value as 121 [11], then the response ratio is 0.95 and the maximum composition error is approximately 1% (Fig. 2). Alternatively, if one adopted the response factor of 90 for 1-chloropropane [11], the response ratio would be 0.74 giving a maximum error of around 8%. Similarly, for a binary mixture containing CBrF_3 , using the predicted value gives a maximum error of 8% whereas assuming the response of CHF_3 leads to an error of 16%.

5. Conclusions

RMR factors for a number of halogenated compounds have been determined by experimental in-

vestigation and compared to values found using a predictive technique. Excellent agreement between experiment and predictions was observed for the gaseous compounds CH_3Cl , CHClF_2 (HCFC-22), C_2HClF_4 (HCFC-124) and C_3F_8 (FC-2-1-8), and close correlation was also observed for CHF_3 (FE-13). Close agreement between experimental and predicted responses was also observed for the liquid species 1,1,1-trichloroethane, *m*-dichlorobenzene, 1-bromo-3-chloropropane, 1-bromo-3-chloro-2-methylpropane and 2-bromopropane. Predicted response factors were also compared to values for larger molecules (C_3 – C_6), including chlorinated, brominated and iodinated halocarbons. The accuracy of the predictive technique was observed to decline as the number of carbon atoms increased and as the halogen composition shifted from chlorine to iodine, suggesting that the model should be a stronger function of molecular size than is presently accounted for. Significant errors were also observed for unsaturated compounds. The level of error was not significantly effected by the presence of mixed halogen atoms, validating the suitability of the prediction for practical refrigerant and fire suppressant analyses. An analysis of the potential errors associated with assuming RMR factors for quantitative analysis was also performed. The errors associated with assuming the response of similar compounds were found to be minimal. For scenarios where there are limited response data available and there is a limited selection of data for similar compounds, one should use the predicted values to minimise composition errors.

Acknowledgements

The authors wish to thank the Fire Protection Association Australia for financial assistance towards this and related projects, and the ongoing support for research into fire safety provided by this not-for-profit technical and educational organisation. We also acknowledge the financial support of the Australian Research Council.

References

- [1] W.A. Dietz, J. Gas Chromatogr. 5 (1967) 68.

- [2] E.F. Barry, D.M. Rosie, *J. Chromatogr.* 59 (1971) 269.
- [3] E.F. Barry, D.M. Rosie, *J. Chromatogr.* 63 (1971) 203.
- [4] D.M. Rosie, R.L. Grob, *Anal. Chem.* 29 (1957) 1263.
- [5] L.W. Flynn, G. Thodos, *AIChE J.* 8 (1962) 362.
- [6] L.S. Tee, S. Gotch, W.E. Stewart, *Ind. Eng. Chem. Fund.* 5 (1966) 356.
- [7] R.C. Reid, J.M. Prausnitz, B.E. Poling, in: *The Properties of Gases and Liquids*, 4th ed, McGraw-Hill, New York, 1987, pp. 656–731.
- [8] C.L. Yaws, in: *Handbook of Chemical Compound Data for Process Safety*, Gulf Publishing Co, Houston, TX, 1997, pp. 5–8.
- [9] R.P. Danner, T.E. Daubert, in: *Manual For Predicting Chemical Process Design Data: Data Prediction Manual*, Design Institute for Physical Property Data, AIChE, New York, 1983, pp. 2A–2G.
- [10] M.J. Lee, H.C. Sun, *Chem. Eng. Commun.* 126 (1993) 205.
- [11] G.R. Jamieson, *J. Chromatogr.* 15 (1964) 260–262.