

Short communication

## Standardless screening of chemical warfare agents based on gas chromatographic data

Andrey S. Lekomtsev\*, Elena P. Vekhter

*Chemistry Department, Research Institute of Hygiene, Toxicology and Occupational Pathology (RIHTOP), Zemljachky st. 12, 400048 Volgograd, Russia*

### Abstract

A method for calculation of the retention time of a compound in a temperature-programmed mode of GC analyses is proposed. The method is based on a detailed consideration of thermodynamics of chromatographic process and account of the actual state of a capillary column. The suggested approach permits estimation of probability of a poisonous agent in tests by means of information stored in the database, eliminating a need for reference standard of such an agent.

© 2003 Elsevier B.V. All rights reserved.

*Keywords:* Retention parameters; Thermodynamic parameters; Sarin; Soman; Sulfur mustard

### 1. Introduction

In present times the probability of chemical warfare agents being used in terrorist attacks has increased greatly. In such incidents it is highly important to identify a toxic agent as quickly as possible. As a rule, the actual analysis is done by gas chromatographic separation of sample components followed by their detection.

An elution time of a substance depends on thermodynamic parameters of interaction with the stationary liquid phase and current conditions of the chromatographic run. For identification of detected components isothermal Kovats indices are widely used [1]. In this approach, the influence of current run conditions on elution time of compounds are taken into account by special standards being mobile reference system. However, for the analyses in a temperature-programmed mode, different temperature dependence of retention parameters of analytes and reference standards are quite often observed [2]. As a result, isothermal and temperature-programmed indices are differed, that considerably complicates identification.

At the same time the general approach for calculation of retention time in a temperature-programmed mode is known [3]. This method is based on consecutive application of thermodynamic relations to elementary mechanisms of chro-

matographic process. It was reported that the use of such approach allows to improve reliability of identification appreciably [4–6].

This work describes a method for calculation of the retention time of a compound in the temperature-programmed mode of GC analyses. The algorithm makes theoretically possible a standardless screening procedure for identification toxic agents in preliminary tests.

### 2. Theory

The method is based on a detailed consideration of thermodynamics of chromatographic process and account of the actual state of a capillary column by means of a special test mixture.

The thermodynamic and chromatographic characteristics of sorbate are described by the equation [7,8]:

$$\ln K = \ln V_g(T) + \ln \rho_L \quad (1)$$

where  $K$  is the partition coefficient between the liquid and gas phases under static conditions,  $\rho_L$  is the density of the liquid phase (g/ml), and  $V_g(T)$  is the specific retention volume (ml/g) at column temperature, not adjusted to 0 °C [9].

Taking into account that for majority of phases numerical value of density lays in a range of 0.9–1.2, the second term of Eq. (1) is in a range from –0.1 up to 0.2. The typical

\* Corresponding author. Fax: +7-8442-391549.  
E-mail address: [a-lek@vlink.ru](mailto:a-lek@vlink.ru) (A.S. Lekomtsev).

values of  $\ln V_g(T)$  are 2–8 units and the amendment on liquid phase density can be neglected.

### 2.1. Estimation of current state of a capillary column

Ageing of a column while in usage, bleeding of liquid phase and periodic cutting off the polluted column inlet result in changes of the mass of phase in column and transport properties of the carrier gas. Therefore, for correct thermodynamic data it is necessary to determine the actual state of the column periodically.

The mass of liquid phase is determined by equation [7]:

$$m_L = \frac{273}{T} \times \frac{V_N(T)}{V_g(T, 0^\circ)},$$

where  $V_N(T)$  is the net retention volume at column temperature, and  $V_g(T, 0^\circ)$  is the specific retention volume at column temperature, adjusted to  $0^\circ\text{C}$  (reference data [10]). For nonpolar and medium polarity phases *n*-alkanes are used as standards.

The transport properties of the carrier gas for a current column are expressed by the dependence of specific hold-up volume  $V_g(T, m)$  from temperature:

$$\ln V_g(T, m) = b_0 + \frac{b_1}{T} \quad (2)$$

This correlation further was used for calculation of specific hold-up volume at current column temperature.

### 2.2. Estimation of thermodynamic retention parameters

The specific retention volume reflects interaction of the solute and the liquid phase at the column temperature  $T$  and depends on temperature as follows:

$$\ln V_g(T) = \frac{\Delta S}{R} + \frac{\Delta H}{RT} \quad (3)$$

where  $\Delta S$  (J/(mol K)) is the solvation entropy, and  $\Delta H$  (J/mol) is the solvation enthalpy.

In case of absence of experimental data, the thermodynamic retention characteristics allow to use a rich possibilities of linear solvation energy relationships (LSER) method [11] to estimate the missing solvation parameters for the solutes and chromatographic phases of different polarity.

### 2.3. Estimation of retention time

The calculation of retention time of the compound at specified linear temperature-programmed modes was carried out by Harris–Habgood method [3], modified according to works [8,9,12].

The parameters were estimated as follows:

- specific flow rate of carrier gas at initial temperature  $T_0$  of the program— $F_g(T_0)$ —was determined by means of hold-up time  $t_m(T_0)$ , measured at this temperature, and

the value of specific hold-up volume at the temperature  $T_0$ — $V_g(T_0, m)$ , calculated on correlation (2):

$$F_g(T_0) = \frac{V_g(T_0, m)}{t_m(T_0)}$$

- specific flow rate of carrier gas at the temperature  $T$ — $F_g(T)$ —was calculated as follows (for helium the exponent is equal to 0.7 [3]):

$$F_g(T) = F_g(T_0) \times \left(\frac{T_0}{T}\right)^{0.7}$$

It is necessary to emphasize, that parameter  $F_g(T)$  has no any physical meaning. It is a mathematical abstraction, introduced for the performance of a dimension rule (as  $V_g(T)$  is the specific value, and  $V(T) = F(T) \times t$ , consequently either  $F(T)$  or  $t$  must be specific).

- “total” specific retention volume at temperature  $T$  was calculated by the association of Eqs. (2) and (3):

$$V_g(T, \text{total}) = \exp\left(\frac{\Delta S}{R} + \frac{\Delta H}{RT}\right) + \exp\left(b_0 + \frac{b_1}{T}\right)$$

The structure of the temperature-programmed mode was set by the table including the following data: a step number ( $i = 1, 2, \dots, n$ ), the step duration ( $t_i$ , min), the program rate ( $r_i$ ,  $^\circ\text{C}/\text{min}$ ), the initial ( $T_{i-1}$ ) and final temperature of the step ( $T_i$ ).

The processing of an  $i$ -step includes:

- (1) Calculation of the part of the column length that was passed by the front of substance ( $z_i/L$ ) (according to the value of  $r_i$ ):

- isothermal mode ( $r_i = 0$ ,  $T = T_i$ )  $z_i/L = F_g(T_i) \times t_i / V_g(T_i, \text{total})$ ; or
- linear programming mode ( $T_{i-1} \rightarrow T_i$ ,  $r_i > 0$ ,  $r_i = \text{constant}$ )

$$\frac{z_i}{L} = \frac{F_g(T_{i-1})}{r_i} \int_{T_{i-1}}^{T_i} \frac{(T_{i-1}/T)^{0.7}}{V_g(T, \text{total})} dT$$

- (2) Summation of the obtained value of  $z_i/L$  with the previous ones and comparison of the sum with 1 is determined the step of substance peak elution. For this step the retention time  $t_R$  is calculated (according to value of  $r_i$ ):

- isothermal step  $t_R = \sum_{j=1}^{i-1} t_j + t_i \left(-\sum_{j=1}^{i-1} \frac{z_j}{L}\right)$ ; or
- linear programming step

$$t_R = \sum_{j=1}^{i-1} t_j + \frac{T_R - T_{i-1}}{r_i}$$

The elution temperature  $T_R$  was found by solving the following integral equation:

Table 1

Thermodynamic parameters and retention times (experimental and calculated) of some chemical warfare agents for different modes of GC analyses (temperature programming: 50 °C–*r*–250 °C)

Substance	−Δ <i>S</i> (J/(mol K))	−Δ <i>H</i> (kJ/mol)	<i>r</i> (°C/min)					
			5		10		15	
			Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
Sarin (GB)	74.6	41.8	4.16	4.21	3.53	3.54	–	3.17
Soman (GD)	73.4	46.6	9.38	9.44	6.59	6.55	5.34	5.27
Sulfur mustard (H)	71.2	48.5	13.29	13.37	8.76	8.74	6.89	6.84

$$\frac{\left(1 - \sum_{j=1}^{i-1} \frac{z_j}{L}\right) r_i}{F_g(T_{i-1})} = \int_{T_{i-1}}^{T_R} \frac{\left[\frac{T_{i-1}}{T}\right]^\circ}{V_g(T, \text{total})} dT$$

This algorithm has shown good results in sophisticated temperature programs [13].

### 3. Experimental

The *n*-alkanes used as reference solutes for gas chromatography were from Merck (Darmstadt, Germany) with stated purity better than 99%. All chemical warfare agents were 95–98% pure (GosNIIOKhT, Moscow, RF).

The chromatographic runs were carried out on 5890 Series II gas chromatograph (Hewlett-Packard, Avondale, PA, USA), equipped with atomic emission detector 5965A (Hewlett-Packard). Fused-silica capillary column (25 m × 0.31 mm i.d.) Ultra-2 (Hewlett-Packard) coated with a film thickness of 0.52 μm liquid phase HP5 (5% diphenyl–95% dimethylpolysiloxane) was used. The columns of Ultra category are characterized as highly inert, a surface adsorption activity is practically absent.

Helium was used as carrier for all the experiments. Gas hold-up time *t*<sub>m</sub> was measured by oxygen peak retention.

The accuracy of experimental retention times were better than 0.01 min (the relative standard deviation did not exceed 0.1%). For predicted retention times the relative standard deviation did not exceed 3%.

The mass of liquid phase was determined for five *n*-alkanes (from hexane to decane) at three temperature levels (60, 80 and 100 °C). The relative standard deviation did not exceed 2%.

For determination of the thermodynamic retention parameters of the substance specific retention volumes were measured at least for six temperatures with a step of 5 °C. Processing of these data according to Eq. (3) has shown an excellent linearity (all the correlation coefficients were better than 0.999).

### 4. Examples

The suggested approach permits an estimation of the probability of the poisonous agents (which is assumed to be present in a specimen) by means of information previously stored in the database eliminating a need for the reference standard of such an agent. Pre-determined thermodynamic parameters of interaction of the substance with the column liquid phase (enthalpy and entropy of solvation) allows to calculate a retention time of the substance in the actual temperature program of the GC analysis by the method described above. Each peak detected in the process of chromatographic separation is checked by this procedure as a possible toxic agent. Real and calculated retention times of some war-gases are shown in Table 1 as examples.

The described method of standardless identification of toxic agents reduces the danger of analytical procedure for lab personnel and allows to perform such an analysis not only in specialized institutions but also in “normal” analytical laboratories in close proximity to an emergency site.

### 5. Conclusions

The method for calculation of the retention time of the compound in the temperature-programmed mode of GC analyses is proposed. The approach permits a rapid estimation of the probability of a toxic agent in tests eliminating a need for a reference standard of such an agent. This feature allows to execute a screening analysis in almost any analytical laboratory.

### 6. Nomenclature

$F_g(T_0)$	specific flow rate of carrier gas at initial temperature $T_0$ of the program
$F_g(T)$	specific flow rate of carrier gas at the temperature $T$

$\Delta H$	solvation enthalpy
$K$	partition coefficient between the liquid and gas phases
$L$	column length
$m_L$	mass of the liquid phase
$r$	temperature program rate
$\Delta S$	solvation entropy
$t_m(T_0)$	hold-up time at the temperature $T_0$
$t_R$	retention time
$T_R$	elution temperature
$V_g(T)$	specific retention volume at column temperature $T$ (not adjusted to 0 °C)
$V_g(T, 0^\circ)$	specific retention volume at column temperature $T$ , adjusted to 0 °C
$V_g(T_0, m)$	specific hold-up volume at the temperature $T_0$
$V_g(T, m)$	specific hold-up volume at column temperature $T$
$V_g(T, \text{total})$	“total” specific retention volume at temperature $T$ (sum of $V_g(T, m)$ and $V_g(T)$ )
$V_N(T)$	net retention volume at column temperature $T$
$z$	distance that was passed by the front of substance

*Greek letter* $\rho_L$  density of the liquid phase**References**

- [1] M.B. Evans, J.K. Haken, J. Chromatogr. 472 (1989) 93.
- [2] C.D. Wick, J.I. Siepmann, W.L. Klotz, M.R. Schure, J. Chromatogr. A 954 (2002) 181.
- [3] W.E. Harris, H.W. Habgood, Programmed Temperature Gas Chromatography, Wiley, New York, 1966.
- [4] Y. Guan, J. Kiraly, J.A. Rijks, J. Chromatogr. 472 (1989) 129.
- [5] Y. Guan, L. Zhou, J. Chromatogr. 552 (1991) 187.
- [6] E.V. Dose, Anal. Chem. 59 (1987) 2414.
- [7] G. Guiochon, C.L. Guillemin, Quantitative Gas Chromatography, Elsevier, Amsterdam, 1988.
- [8] S.Yu. Kudryashov, L.A. Onuchak, V.A. Davankov, Russ. J. Phys. Chem. (Engl. Transl.) 76 (2002) 833.
- [9] V.A. Davankov, Chromatographia 44 (1997) 279.
- [10] C.F. Chien, M.M. Kopečni, R.J. Lanb, J. High Resolut. Chromatogr. Chromatogr. Commun. 4 (1981) 539.
- [11] C.A. Graffis, D.S. Ballantine, J. Chromatogr. A 946 (2002) 185.
- [12] V.A. Davankov, L.A. Onuchak, S.Yu. Kudryashov, Yu.I. Arutyunov, Russ. J. Phys. Chem. (Engl. Transl.) 73 (1999) 1602.
- [13] A.S. Lekomtsev, E.P. Vekhter, A.V. Nazarkin, I.E. Pildus, Ecol. Chem. 6 (1997) 120 (in Russian).