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GCSIM: a gas–liquid chromatography simulator for educational purposes

J. C. Reijenga

Laboratory of Instrumental Analysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven (Netherlands)

ABSTRACT

A gas–liquid chromatography simulation program was written for personal computers. A graphic display of a chromatogram is shown by the simulator. The program can be used to illustrate various effects in gas chromatography for demonstrations or lectures. In addition, it can be used as an advanced supplemental instrument simulator in a practical course. Variables include column length, inlet pressure, phase ratio, temperature (both isothermal and linear programming) and detector attenuation. Additional parameters offer a choice between packed and capillary columns, two different detectors, two stationary phases and two carrier gases. The sample composition can be changed to include any solvent and up to six components from a library of 75 at different concentrations.

INTRODUCTION

Teaching chromatography implies the description of a number of phenomena occurring at the interface of the mobile and stationary phases: phase equilibria, concentration distributions and other effects that can all be put into equations. This latter aspect provides a sound basis of the principles of chromatography. Attractive though this may seem, a lot of imagination is necessary to really understand what is happening in a column. For this reason, at the Faculty of Chemical Engineering of the Eindhoven University of Technology, we have decided to introduce chromatography in a practical course for first-year students. First, column chromatography and thin-layer chromatography (TLC) of dyes are dealt with in a qualitative manner. Subsequently, a gas chromatography (GC) course is given. In this case, with the TLC results in mind, GC is more readily understood. A minimum of theory, however, is required before the use of a microsyringe can be considered.

A gas chromatography simulator was written for personal computers. The aim of the program is twofold. First, it can be used, in an introductory lecture, to visualize various effects associated with the variables that are at our disposal on a modern gas chromatograph. Second, the simulator can be used as an additional instrument in a practical course.

A number of simulators of chromatographic separations have been described [1,2]. The high-performance liquid chromatography simulator from the SERAPHIM project is attractive, especially for a practical course on reversed-phase liquid chromatography. Another program is aimed at solving a specific separation problem (PROTEINS; IRL Press, Eynsham, Oxford, UK). This simulator combines a number of pretreatment, separation and identification techniques with the purpose of isolating a protein from a mixture.

Of the GC simulators available, GLCSIM (A. B. de Vries, Werkgroep BOS, Zuidhorn, Netherlands) contains a limited number of sample components, a considerable number of stationary phases and variable retention times. Its limitation is that it only works with packed columns, under isothermal conditions, with a single detector. Another GC simulator, distributed in the SERAPHIM project, seems restricted to the evaluation of column packings (J. K. Hardy, University of Akron, Akron,

OH, USA). A severe drawback of the SERAPHIM products is that they are distributed as ASCII sources for GWBASIC, a programming tool unsuitable for structured programming.

Our aim was therefore to write a simulator with relatively advanced features, as a stand-alone, compiled EXE file. Also, the program should not be too choosy regarding the hardware required. As usual while programming, specifications grew as time went by. One requirement, however, was adhered to: a simulator for educational purposes and not an accurate predictor of experimental results. We are aware of the existence of simulators that claim to be in compliance with present state-of-the art in GC retention modelling [3], mostly for optimization purposes [4]. In those instances, the simulator is used as a research tool. This paper describes GCSIM, a teaching tool.

EXPERIMENTAL

Hardware and software

The program runs on any IBM-compatible personal computer of the PC, XT or AT type, operating under DOS operating system version 3.2 or higher with 640 kbyte of memory. A single disk drive of 3.5 or 5.25 in. is sufficient. A graphics adapter and monitor are required, either monochrome or colour. The program does not use colours and automatically adapts to any of the following graphics cards: EGA, CGA, AT&T 6300 and Hercules. If a mathematical coprocessor is present, this greatly improves the calculation speed; otherwise the coprocessor is emulated. An XT-type PC with a coprocessor is preferred over an AT type without. There is no mouse support. An IBM graphics printer is optional, with the restriction that not all graphics cards allow screen dumps to be printed.

The program was written in Microsoft Quickbasic version 4.5 and compiled into a stand-alone EXE file which can be run independently from the Quickbasic programming environment. Details of the availability of the program can be obtained form the author.

In addition to the program GCSIM, the program diskette contains six help files that can be accessed from the program. Finally, there is a data file with retention data for 75 sample components on two stationary phases as a function of temperature. The program is self-explanatory. The available course manual contains a description and a number of experiments.

The model

The chromatographic model on which the simulator is based is simplified but straightforward [5]. Values of constants in the equations are mostly derived from experimental data. The gas compressibility factor j is assumed to be unity throughout the model. The gas velocity u is calculated from the pressure gauge reading P and the column length L:

$$u = c_1 P/L \tag{1}$$

In which the constant c_1 depends on the carrier gas and the type of column. The retention time of the unretained component t_0 is then calculated with

$$t_0 = L/u \tag{2}$$

The velocity dependence of the plate height H is described by a three-parameter model:

$$H = c_2 + c_3 u + c_4/u \tag{3}$$

Constants in this equation depend on the column type and carrier gas. The temperature dependence of the net retention volume V_N is approximated by a two-parameter model [2]:

$$\ln V_N/\beta = c_5/T + c_6 \tag{4}$$

where β represents the phase ratio V_m/V_s.

Neglecting gas compressibility, the net retention volume V_N can be rewritten as:

$$V_N = k V_m \tag{5}$$

Combination of eqns. 4 and 5 gives

$$\ln(k V_m) = c_5/T + c_7 \tag{6}$$

where k is the capacity factor. From the literature we obtained tabulated values of V_g, the specific retention volume, at different temperatures and for two stationary phases [6]. The specific retention volume is defined as the net retention volume per unit mass of stationary phase W_s:

$$V_g = V_N \cdot 273/T/W_s \tag{7}$$

where T is the absolute temperature.

Combination of eqns. 5 and 7, with $W_s = \rho_s V_s$, yields

$$V_s = k\beta 273/\rho_s/T \tag{8}$$

This relationship is now approximated by

$$k = V_g(T)/\beta \qquad (9)$$

thus simplifying subsequent calculations to a considerable extent. Accurate prediction of experimental retention times, which is not the aim of the simulator, is not possible, mainly owing to this last approximation which introduces a slight systematic error because $273/\rho_s/T$ is usually less than unity. Finally, it is assumed that k fits a two-parameter model similar to that of eqn. 4:

$$k = \exp(c_8/T + c_9) \qquad (10)$$

The retention time t_R is then calculated using

$$t_R = t_0(1 + k) \qquad (11)$$

The peak width σ is obtained from

$$\sigma = t_R/\sqrt{N} \qquad (12)$$

The detector sensitivity and selectivity are modelled as follows: the thermal conductivity detection (TCD) response is the same for all sample components and in addition depends on the carrier gas. The flame ionization detection (FID) response is proportional to the molecular weight of the sample component and the gas velocity u.

The algorithm

In the algorithm for the calculation of retention, values of k at two reference temperatures are first calculated from V_g using eqn. 9, then values of c_8 and c_9 are calculated using eqn. 10, which is finally used to calculate k at the desired temperature.

For temperature programming, retention times are calculated by summation of time increments (and corresponding temperature and column length increments) of 5 s until the column outlet is reached. The peak width in temperature programming is approximated by the width of the peak if it were to have eluted isothermally at the programmed elution temperature.

The algorithm for the calculation of chromatograms consists of the following procedures. On start-up of the simulator, a baseline with random white noise is generated once. During a session with the simulator this baseline is used throughout, because random generation is time consuming, especially for normally distributed noise. In order to maintain the random character of the noise, the noisy baseline is randomly shifted with respect to the resulting chromatogram each time a new chromatogram is calculated. For each component in the sample, k, t_R and σ are first calculated as described in the previous section. For each sample component, the corresponding peak is now added to the baseline if t_R is within the time interval displayed. Of each of these peaks only a width of 8σ units around the top is considered, thus reducing the calculation time to a considerable extent. The resulting chromatogram is now displayed in the graphics window, using the detector attenuation as a scaling factor.

Performance of the simulator

The gas chromatography siumulator contains a large number of instrumental parameters. For educational purposes a choice was made for two distinctly different stationary phases in terms of polarity. Also, comparison of capillary and packed columns was considered an important feature. The latter are especially useful for illustrating peak broadening in a graphic presentation. Table I lists the operational range of all experimental parameters.

The simulator screen (Fig. 1) consists of graphical and numerical information, with a main menu command line at the top of the screen. The chromatogram displayed is limited to a time interval of *ca.* 21 min (23 min for Hercules graphics), the time resolution of one screen pixel corresponding to 2 s. This resolution seems poor for capillary GC, but was found to represent an attractive compromise between calculation time and amount of information contained in one graphics screen. In addition to the sample component peaks, a solvent peak and the unretained peak are shown. Recalculation and display of a new chromatogram is immediately executed, following a change in any of the instrumental or sample parameters.

The lower left-hand corner of the screen gives information on instrumental parameters such as column, detector and carrier gas. Sample information is given at the lower right-hand corner: component name, k, concentration and peak area are given. In between these two blocks, some additional information on instrument performance is given: retention time of the unretained component, gas velocity, plate number and resolution if there are two sample components.

TABLE I

OPERATIONAL RANGE OF EXPERIMENTAL PARAMETERS OF THE SIMULATOR

Parameter	Operational range
Packed column	Length 1–5 m in 1-m increments I.D. 2 mm Phase ratio 8–20 in increments of 1
Capillary column	Length 10–30 m in 10-m increments I.D. 0.35 mm Phase ratio 80–400 in increments of 10 Injection splitting ratio 50–200 in increments of 10
Carrier gas	Nitrogen or helium
Detection	FID or TCD (packed only) Attenuation 1–8192 in increments of a factor of 2 Linear or logarithmic display Rectangular noise filter width 1, 3, 5, 7, 9 screen resolution units
Temperature	50–200°C in increments of 2°C Isothermal hold time 0–9 min in increments of 1 min Programme 0–9°C/min in increments of 1°C/min
Injection	Choice of any sample component as solvent Concentration of sample components 0–10 000 ppm Volume 0–2 μl in 0.1-μl increments
Retention time	0–21 min (23 min for Hercules)

The main menu, always visible in line 1, gives access to a number of pull-down submenus by means of the key corresponding to the first capital letter of the main menu item. Cursor (arrow) keys can be used in the pull-down menus in addition to the capital letter keys.

Table II lists all submenus, some of which are again followed by a further submenu, etc.; for instance, SLC (System Load Chromatogram) loads a chromatogram previously stored.

Registration of operation

When used in a practical course, information on how the simulator is used by the student can be valuable to the teacher. To this end, GCSIM stores all information on commands used in a sequential ASCII file with extension .REG. This may be especially useful in optimizing studies, as will be shown in the next section. The contents of the .REG file will look like this

90_TG:9
12_SLS:butanols

In this example the user has decided after 90 s to change temperature programming to a gradient of 9°C/min and 12 s later decided to load a sample called "butanols".
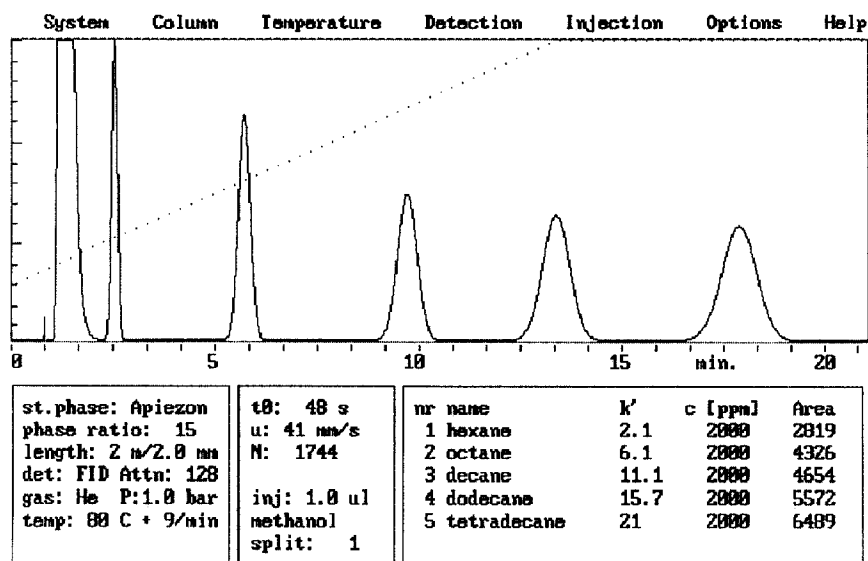

Fig. 1. A typical GCSIM screen with the main menu on the top line. Instrumental and sample parameters are given below the chromatogram. See text for details.

TABLE II

SUBMENUS TO THE MAIN MENU OF THE SIMULATOR

Further submenus are denoted by three periods.

System	Column	Temperature	Detection	Injection	Options	Help
Load ...	column Type...	Temperature	Type	Components...	Disturbance.	Main
Save ...	column Length.	Isothermal	Attenuation	coNcentrations	Variance...	Options
Dos shell	Phase type...	Gradient	Filtering	Solvent...	Quality	Score
Quit...	phase Ratio			Volume	Scaling ...	sPecs.
	Gas type ...			splitting Ratio	Inject...	sImul.
	gaS pressure			Delete all	Erase...	
					sCore...	
					options Help	

Any text editor can be used to page through the registration files. When upon start-up of the simulator an identification number is given, the registration filename contains this identification number, so that individual results can be stored separately.

What is not simulated and why

Computer simulation of instumental analysis offers the possibility of changing parameters that are normally not variables: noise, drift, tailing and spikes can be changed at will (Fig. 2). This does not imply that an instrument simulator should always have better specifications than the original instrument.

A number of features were considered and omitted for two reasons: their effect was of minor influence and they would not additionally contribute to the aim of the simulator. These features include dependence of the plate height equation on k, additional selective detectors, mutual interference of sample components, detector non-linearity, injec-

tion errors, stationary phase bleeding, sample component condensation and more stationary phases.

Concerning the range allowed for different variables, values can in principle be chosen that would in practice lead to unsatisfactory performance. Consider, for instance, the possibility of heavily overloading a capillary column with tetradecane at 50°C. This has not been prohibited by the simulator as good use should be made of the possibility to make mistakes, an obvious advantage over a real instrument. The intelligence required by the program to prohibit such actions by the user is considerable and should be thoroughly tested. Otherwise it would severely limit the flexibility of the program.

RESULTS AND DISCUSSION

Use of GCSIM in lectures and demonstrations

Some features of the simulator were incorporated with the purpose of speeding up the demonstration of various effects in GC. Load and Save options enable the user to prepare examples to illustrate these effects. The quickest way to show previously prepared results is by means of Save Chromatogram and Load Chromatogram as nò calculation is necessary. A chromatogram thus stored takes up less than 3 kbyte of memory. Details on how the chromatogram was obtained are not saved, however, except in the .REG file.

In the case of Save/Load of Parameters or Samples, however, these details are included but recalculation prior to display is necessary. When using a coprocessor this takes only a few seconds. Without a coprocessor and calculating temperature pro-
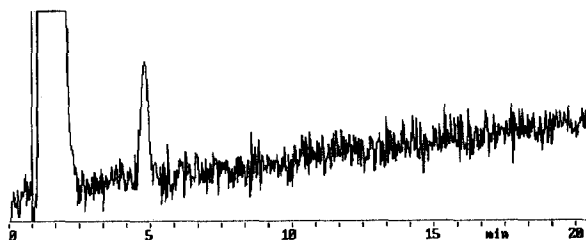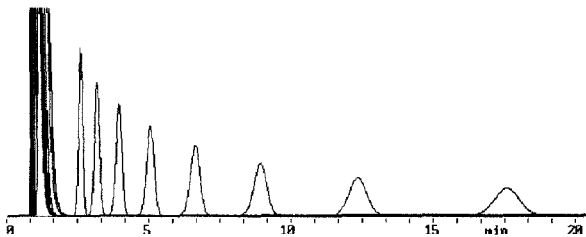

Fig. 2. A number of optional parameters, such as noise, drift, spikes and tailing, can produce complicated looking chromatograms that can be used to illustrate aspects of detection limits.

Fig. 3. With the Option Erase off, chromatograms can be super-imposed. The example shows the influence of temperature in 10°C increments on the retention of octane on a packed Apiezon column of 2 m length, with helium at 1 bar inlet pressure.

Fig. 5. As Fig. 4, with the same elution order but higher selectivity using Carbowax as a stationary phase under otherwise identical conditions.

gramming, calculation times of up to 20 s can be a problem in an otherwise rapid demonstration. Saving instrumental parameters or sample compositions requires less than 1 kbyte of memory each. A collection of most commonly used examples can therefore be included on the GCSIM diskette.

For comparison of chromatograms, the option Erase may be useful. In this instance, the previously shown chromatogram is not erased. Fig. 3 shows an example of the non-linear dependence of k on T. In this example octane is analysed at different temperatures. Also illustrated by Fig. 3 is the principle of peak broadening and decreasing peak height at increasing retention times. At low concentrations, the detector attenuation can be decreased to visualize the disappearance of the peak into the noise on decreasing the temperature. The application of a simple rectangular moving average noise filter can be shown to give some improvement of the signal-to-noise ratio.

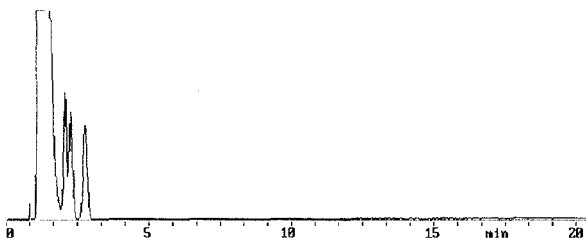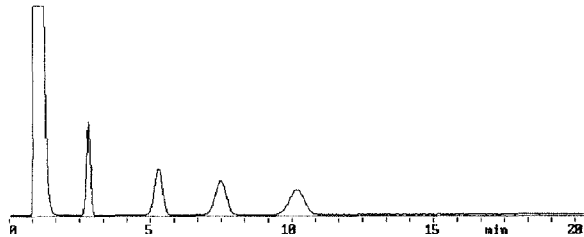A third example is shown in Figs. 4 and 5 where, at the touch of a key, the selectivity of the station-

ary phase is illustrated by the analysis of butanols. The elution order is the same (it would have required a number of experiments to verify this in reality), but the selectivity is greatly improved when switching to a polar stationary phase.

A comparison of packed and capillary columns easily shows the effect of plate number and phase ratio on the elution profile of a mixture. In this instance, the other instrumental parameters switch to their default values, which are different for packed and capillary columns.

Use of GCSIM in a practical course

This computer program is not intended to replace all gas chromatographs in the instruction laboratory by PC's, although this would certainly be cheaper. It will be shown, however, that the simulator as a supplemental tool can provide experimental results in a very short time. In a try-out at the Eindhoven University of Technology, fifteen students in their second year first attended a 6-h series of lectures on GC theory, followed by a practical course using the simulator for a total of 7 h during two afternoons.

The practical course consisted of a number of experiments with GCSIM. The procedure was as follows. A course manual contains short descriptions of certain phenomena in GC and corresponding experiments to be carried out. First, instrumental parameters for that experiment are loaded, then a sample composition is chosen. The actual experiment consisted of changing certain instrumental and sample parameters. The values obtained are then put in a graph, using forms provided. The results are interpreted by answering a few questions on the subject.

The following experiments were included: (1) de-

Fig. 4. Analysis of tert.-, sec.-, iso- and n-butanol on a 2-m packed Apiezon column at 90°C, with helium at 1 bar inlet pressure and FID.

pendence of k on T; (2) calibration, dynamic range, detection limit; (3) effect of phase ratio on retention; (4) effect of plate number on resolution; (5) effect of stationary phase type on selectivity; (6) analysing homologous series; (7) specific detector response for FID and TCD; (8) effect of linear gas velocity on plate height; (9) optimizing separation with and without temperature programming; and (10) comparison of packed and capillary columns. These are only some of the possibilities for practical course subjects. Tables I and II can be used to design additional subjects.

As an example, a description of experiment 4 from the course manual is given below:

"As indicated in the lecture, a difficult separation requires more plates than an easy one. The concept of Resolution was introduced to quantify the separation of two peaks at given k values (Selectivity). Load parameter file 4 (this is a short packed column) and choose a sample consisting of 10 ppm each of 3-hexanol and 2-hexanol dissolved in acetone. The resolution will now be measured as a function of the plate number. The plate number depends on the column length and the linear gas velocity. Change the column length and gas inlet pressure in such a range that plate numbers between 500 and 2000 are obtained.

Plot the results of resolution and plate number on sheet no. 4, which has double log scales (see Fig. 6).
Answer the following questions:

—which two parameter exponential relation describes this dependence?
—what plate number would be required for unit resolution?"

The resulting graph fits a straight line that can be extrapolated to unit resolution. Linear curve fitting yields a value of $ca.$ 0.5 for the slope of the line, which means resolution improves with the square root of the plate number, as expected.

As a second example of a practical course subject, an optimization experiment is presented. Here, the sequence of loading parameters first, sample next is important. The underlying idea is that the initial conditions are to be identical for all students and of course far from optimized. The registration files are used here for two purposes: (1) it can be checked if the course manual instructions were adhered to and (2) exact reconstruction of the actions by the students is possible.

As a first optimizing experiment, only a limited number of parameters were allowed to be changed. The reason was that otherwise most students would very soon switch to a 30-m capillary with temperature programming, thus short-cutting the optimization process. In most instances, this would also lead to an over-specified instrument.

In the initial chromatogram, some peaks are outside the time window displayed and others overlap. At this stage, additional information on sample component properties could be given. In our try-
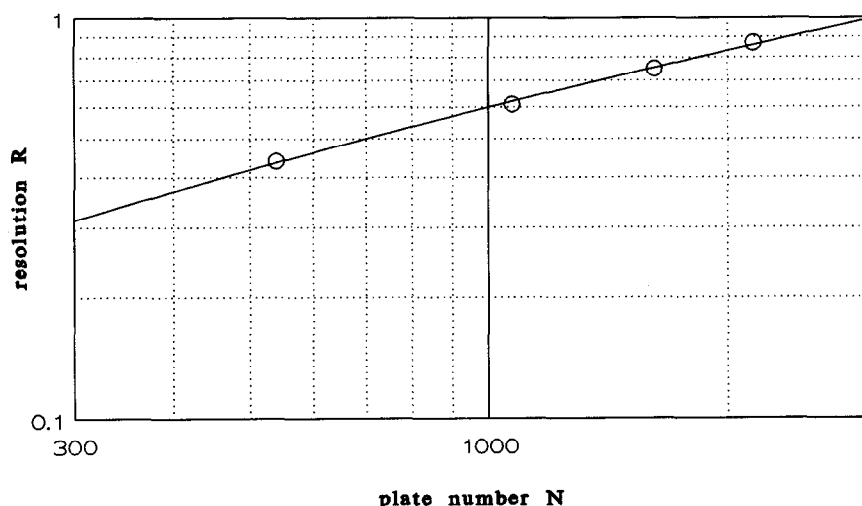

Fig. 6. Resolution of 3- and 2-hexanol on a packed Carbowax column as a function of plate number.

out, we decided not to do this, resulting in a more or less trial-and-error approach. The choice of the parameters changed was shown to give a good indication of whether the concept of GC selectivity was understood.

Good first guesses were (if allowed): a stationary phase change and a steep temperature gradient, provided the initial linear velocity was not too low. Less smart students were seen playing with parameters of minor importance instead. In this context, one additional option should be mentioned, namely the scoring facility, which permits the introduction of a game element in optimizing experiments. With the scoring option turned on, each change in a parameter results in a change in the score variable, shown at the lower left-hand corner of the screen. Some changes, however, are more expensive than others. Evidently, selecting a capillary column is more expensive than doubling the length of a packed column. If, in addition to a good separation, a minimum score is required, students are forced to think before acting.

CONCLUSIONS

It was shown that the instrument simulator GCSIM can provide graphic illustrations of numerous phenomena in GC, for both lectures and demonstrations but also for written course material. A large number of experiments can be simulated in a very short time when used in a practical course. However, we advise against replacing all gas chromatographs in the instruction laboratory. As a first acquaintance with instrumentation, we recommend that the students perform a few syringe injections into a simple gas chromatograph, and wait for peaks to appear ("Sir, is this the last one?"). Waiting for the end of chromatograms takes a lot of practical course time, a problem largely eliminated by additional use of GCSIM in such a course.

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