Effects of column parameters on optimization of gas chromatography/mass spectrometry

ARTICLE *in* ANALYTICAL CHEMISTRY · JULY 1982

Impact Factor: 5.64 · DOI: 10.1021/ac00245a010

3 AUTHORS, INCLUDING:

Eva Matisová
Slovak University of Technology in Bratislava
5 PUBLICATIONS **12** CITATIONS
SEE PROFILE

Ernst Kenndler
University of Vienna
258 PUBLICATIONS **6,364** CITATIONS
SEE PROFILE

Effects of Column Parameters on Optimization of Gas Chromatography/Mass Spectrometry

Josef F. K. Huber,* Eva Matisova,[1] and Ernst Kenndler

Institute of Analytical Chemistry, University of Vienna, Waehringerstrasse 38, A-1090 Vienna, Austria

The optimization of the gas chromatography/mass spectrometry system with direct coupling interface is discussed with respect to component resolution and mass sensitivity. A theoretical treatment is given which leads to an optimization factor combining the relevant process variables. This optimization factor can be made a maximum by operating the chromatographic column at the flow velocity giving the minimum theoretical plate height and matching the column outlet flow rate to the maximum allowable inlet flow rate of the mass spectrometer by adjusting the column cross sectional area. The theoretical prediction is verified experimentally for packed bed columns of different diameters and an open tubular column. Both, a packed bed column of 1 mm i.d. and an open tubular column of 0.3 mm i.d., match the fixed inlet flow of the mass spectrometer at about the flow velocity of the theoretical plate height minimum. The value of the optimization factor is found to be about the same for both columns if split sampling with a split ratio of 1/50 is used for the open tubular column. With splitless sample injection the open tubular column would be superior mainly due to its smaller flow cross sectional area.

Selectivity, sensitivity, and noise are the most important static system characteristics in analytical chemistry. In view of these characteristics, GC/MS, the on-line combination of gas chromatography, GC, and mass spectrometry, MS, is the most powerful tool in the chemical analysis of volatile samples. It combines a high-performance separation method with a high-performance measuring technique. GC/MS can be used in the selected ion monitoring mode for quantitative analysis and identification and in the scanning mode for structure elucidation. Since its introduction in 1957 (*1–5*) GC/MS has developed to a very high level of performance combining high selectivity, high sensitivity, and low noise level. In the scanning mode it has the highest information content (*6*) of all identification and structure elucidation methods for organic compounds, in the selected ion monitoring mode it has a very low detection limit on the order of picograms and below. It has proved to be the ideal method for the analysis of trace components in complex mixtures.

The application of GC/MS is limited by the volatility and thermal stability of the sample. This limit can be pushed up to some extent by derivatization of the sample to form sufficiently volatile and stable products. Beyond its limit of application GC/MS is supplemented by LC/MS, the combination of liquid chromatography, LC, and mass spectrometry. LC/MS is also an alternative to derivatization GC/MS.

In GC/MS as well as in LC/MS the interfacing of both unit operations, having different characteristics, is a crucial problem, which has been solved to a large degree in GC/MS and is still under development in LC/MS (*7, 8*). The work concerning the on-line coupling of GC and MS was recently reviewed in two papers (*9, 10*). The different types of interfaces proposed for the on-line coupling of GC and MS are shown schematically in Figure 1 and their performances are given in Table I. So far the efforts to develop an optimal GC/MS system have been focused on the mass spectrometer and interface design. Little attention has been given to the possible adjustment of the gas chromatographic column.

In the application of GC/MS in trace analysis it is essential to optimize the system with respect to separation performance and detection sensitivity. This paper discusses the effect of the chromatographic column, especially the column diameter, on the detection limit of GC/MS systems with open direct coupling of GC and MS.

THEORY

Interfacing Criteria. In isocratic elution chromatography a dilution of the sample occurs during the separation process. The maximum concentration (peak height), $(c_i^{(m)})_{Lmax}$, of a component, i, in the mobile phase, m, at the end, L, of the chromatographic column is described by the following equation (*11*):

$$(c_i^{(m)})_{Lmax} = \frac{Q_i}{(2\pi)^{1/2}\epsilon_m A(H_i L)^{1/2}(1 + \kappa_i)} \quad (1)$$

in which Q_i = injected amount of component i, A = cross sectional area of the column, ϵ_m = fraction of the cross section occupied by the mobile phase m, L = length of the column, H_i = theoretical plate height of the column for component i, and κ_i = capacity factor of the component i. Equation 1 is valid under the assumption that the elution peak approaches a Gaussian shape and that the peak width is created by the chromatographic process only. If the sample is limited in size, Q_i, the only free variable for maximizing the height of the elution peak, $(c_i^{(m)})_{Lmax}$, is the column cross sectional area, A. All other variables cannot be chosen independently since they occur also in the equation for the chromatographic resolution, R_{ji}, of two components j and i, which for negligible extracolumn effects reads (*12*)

$$R_{ji} = \frac{t_{Rj} - t_{Ri}}{\sigma_{tci}} = (r_{ji} - 1)\frac{\kappa_i}{(1 + \kappa_i)H_i^{1/2}}L^{1/2} \quad (2)$$

where t_{Rj}, t_{Ri} = retention times of the components j and i ($t_{Rj} > t_{Ri}$), σ_{tci} = standard deviation of the elution peak of component, i, resulting from the chromatographic process, $r_{ji} = \kappa_j/\kappa_i$ = selectivity coefficient of the column for the components j and i. From eq 1 and 2 it can be seen that the peak height can be increased by decreasing the column cross sectional area without affecting the chromatographic resolution of the components.

This conclusion holds up only to the point where the extracolumn effects to the peak width become significant. In general, the observed variance, σ_{ti}^2, of the signal peak of a component, i, is composed of a number of increments which can be combined as follows (*13*)

$$\sigma_{ti}^2 = \sigma_{tci}^2 + \sigma_{te}^2 \quad (3)$$

where σ_{tci}^2 = contribution to the peak variance caused by the

[1] Permanent address: Slovak Technical University, Faculty of Chemistry, Department of Analytical Chemistry, Bratislava, CSSR.

0003-2700/82/0354-1297$01.25/0

Table I. Performances of the Different Types of GC/MS Interfaces

characteristics	performance for the type of interface: closed direct coupling	coupling via enrichment device (separator)	open direct coupling
reduction of chromatographic resolution	significant (if the stationary phase mass transfer dominates the theoretical plate height)	in most types insignificant	negligible
enrichment or dilution factor	1	~100	≤1, depending on flow rate
transfer efficiency (split ratio) [%]	100	≥50	≤100, depending on flow rate
adsorption and decomposition effects	negligible	small to significant depending on material and surface area	negligible

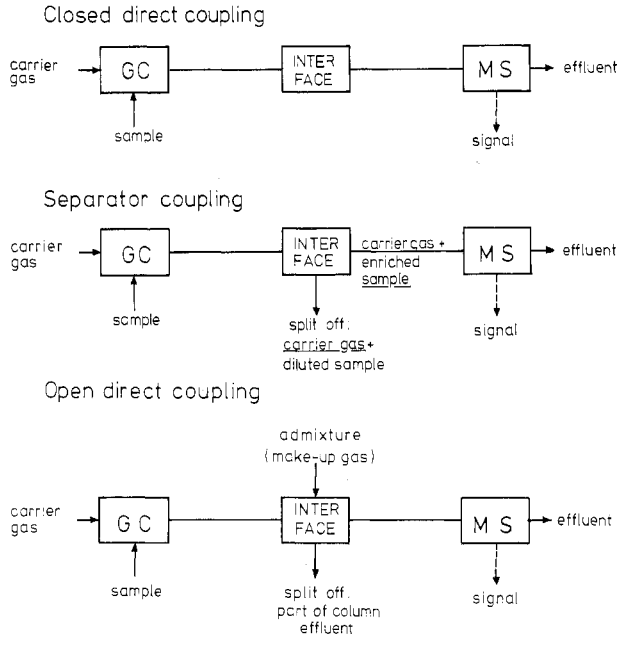

Figure 1. Schematic representation of the three different types of on-line coupling of gas chromatography and mass spectrometry.

chromatographic process in the column and σ_{te}^2 = extracolumn contribution to the peak variance caused by the sample volume and the processes in the sampling device and the detection unit. Substitution of σ_{ti}^2 in eq 2 by eq 3 leads to the following expression (*14*)

$$R_{ji} = \frac{t_{Rj} - t_{Ri}}{\sigma_{tci}} \frac{1}{(1 + \sigma_{te}^2/\sigma_{tci}^2)^{1/2}} \quad (4)$$

According to this equation the resolution approaches the maximum value, $(t_{Rj} - t_{Ri})/\sigma_{tci}$, if $\sigma_{te}^2 \ll \sigma_{tci}^2$. The contribution generated in the extracolumn volume can be described by the expression

$$\sigma_{te}^2 = V_e^2/w_e^2 N_e \quad (5)$$

in which w_e = flow rate, V_e = extracolumn volume, and N_e = theoretical plate number of the extracolumn volume defining its mixing characteristics.

It follows that the extracolumn contribution, σ_{te}^2, of a given chromatograph increases relative to the column contribution, σ_{tci}^2, with decreasing cross sectional area of the chromatographic column because of the resulting decrease of the flow rate. Consequently the total resolution decreases with decreasing column cross sectional area beginning from a given value of the cross sectional area depending on the instrument design.

In principle the mass spectrometer responds linearly to the input mass flow of sample up to a limit given by the ion source pressure. Therefore the response curve of the mass spectrometer for a given sample concentration ascends linearly with the inlet flow rate up to a given limit. Above this limit the response curve reaches quickly a maximum and drops steeply with further increasing flow rate. For maximum sensitivity the mass spectrometer should be operated at the input flow rate corresponding to the upper limit of the linear range. At fixed input flow rate the mass spectrometer responds to the concentration of sample. From the analytical point of view the mass spectrometer should be operated within its linear range, where response is described by the expression

$$y_M = y_{Mo} + S_M c_M \quad (6)$$

where y_M = output signal of the mass spectrometer, y_{Mo} = background output signal of the mass spectrometer, S_M = sensitivity of the mass spectrometer for a given component, c_M = concentration of the component in the ion source of the mass spectrometer. The concentration, c_M, in the ion source of the mass spectrometer depends under stationary conditions on the inlet concentration, the inlet flow rate, and the outlet flow rate and is given by the mass balance equation

$$0 = \frac{dc_M}{dt} V_M = c_{MO} w_{MO} - c_M w_M \quad (7)$$

where V_M = volume of the ion source of the mass spectrometer, w_{MO} = flow rate at the inlet of the mass spectrometer, c_{MO} = concentration at the inlet of the mass spectrometer, w_M = flow rate at the outlet of the ion source, and c_M = concentration at the outlet of the ion source of the mass spectrometer. Equation 7 assumes that the total pressure drop occurs over the inlet tubing and the concentration and flow rate are constant in the ion source and equal to the values at the ion source outlet.

In general, the ion source is operated at a pressure on the order of 10^{-8} bar, the inlet pressure of the mass spectrometer being about 1 bar. Consequently the ratio of the concentrations at the inlet and the outlet of the mass spectrometer and the ratio of the outlet and the inlet flow rates are about 10^8.

The general flow scheme of the GC/MS system is shown in Figure 2. In the case of the open direct coupling the interface consists essentially of the outlet tubing of the chromatograph and the inlet tubing of the mass spectrometer separated by a narrow slit, which is scavenged by helium of 1 bar. In such an arrangement the inlet flow rate of the mass spectrometer is fixed for given inlet capillary dimensions, temperature, and carrier gas. This means that the total sample is fed to the mass spectrometer only if the inlet flow rate of the mass spectrometer is equal or below the column outlet flow rate. For larger inlet flow rates of the mass spectrometer a part of the sample is split off and only a fraction according

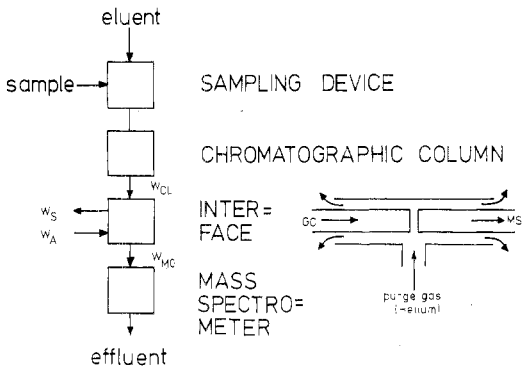

Figure 2. Flow diagram of the GC/MS combination with open direct on-line coupling. w_{CL} = flow rate at the outlet of the chromatographic column, w_{MO} = flow rate at the inlet of the mass spectrometer, w_S = flow rate of interface split stream, w_A = flow rate of admixture gas.

to the split ratio reaches the ion source. On the other hand, if the column outlet flow rate, w_{CL}, is smaller than the fixed mass spectrometer inlet flow rate, w_{MO}, the sample is diluted by helium and the sample concentration, c_{MO}, at the mass spectrometer inlet decreases. According to Figure 2 the splitting or dilution of the sample in the interface is determined by the following equations:

$$w_{MO} = w_{CL} - w_S + w_A = \text{constant} \tag{8}$$

$$c_{MO} = c_{CL}\frac{w_{CL} - w_S}{w_{MO}}$$

where c_{CL} is the concentration at the column outlet, and w_S and w_A are the flow rates of the split stream and admixture stream, respectively. Combining eq 1 and 8 and considering that w_{MO} is constant leads to the following expression for the concentration at the inlet of the mass spectrometer which determines the magnitude of the output signal according to eq 6 and 7

$$c_{MOi} = \frac{\beta_S\beta_D Q_i}{(2\pi)^{1/2}\epsilon_m A(H_i L)^{1/2}(1 + \kappa_i)} \tag{9}$$

in which β_S is the split factor at the sample introduction and $\beta_D = c_{MO}/c_{CL} = (w_{CL} - w_S)/w_{MO}$ is the dilution factor resulting from the admixture of make-up gas at the interface.

Optimal Matching of the Column. The aim of the optimization in GC/MS for trace analysis is to meet both requirements, high resolution, R_{ji}, and low sample dilution, $Q_i/(c_{MOi})_{max}$. For the purpose of optimization the following target function can be defined using eq 2 and 9.

$$\frac{R_{ji}(c_{MOi})_{max}}{Q_i} = \frac{(r_{ji} - 1)}{(2\pi)^{1/2}}\frac{\beta_S\beta_D\kappa_i}{\epsilon_m A H_i(1 + \kappa_i)^2} \rightarrow \text{maximum} \tag{10}$$

The value of this target function can be set to a maximum by choosing the appropriate working conditions.

The selectivity coefficients, r_{ji}, of the successively eluting pair of components should be adjusted to be as large as possible which can be done via the chemical nature of the phase system and the temperature. For complex mixtures a compromise has to be found for all pairs of components. It is likely, however, that the selectivity coefficient cannot be made large enough for all pairs of compounds. The remaining term in eq 10 can be used as optimization factor, F_{opt}, which has to be made a maximum

$$F_{opt} = \frac{\beta_S\beta_D\kappa_i}{\epsilon_m A H_i(1 + \kappa_i)^2} \rightarrow \text{maximum} \tag{11}$$

This can be achieved in the following way: (1) The sampling split ratio, β_S, should have the maximum value of 1, i.e., inlet splitting should be avoided. (2) The theoretical plate height should be minimized. The minimum of the theoretical plate height is achieved at a given mobile phase velocity, u. (3) The factor $\kappa_i/(1 + \kappa_i)^2$ has its maximum value at $\kappa_i = 1$. The capacity factor can be adjusted by the phase ratio and can be made optimal for the separation of only one pair of components of a given mixture. (4) The volume fraction, ϵ_m, of the column filled by the mobile phase, m, is relevant for packed columns. It varies only slightly between 0.6 and 0.8 depending on the porosity of the solid support and the degree of the loading with stationary liquid. For open tubular columns ϵ_m obviously equals one. (5) Finally, the cross sectional area, A, of the column has to be chosen. It influences the ratio β_D/A which is constant up to given value of A.

Above this value the ratio decreases according to $\beta_D/A = 1/A$. At the point up to which the ratio β_D/A remains constant the outlet flow rate of the column matches the fixed inlet flow rate of the mass spectrometer. Below the matching point a decrease of the cross sectional area of the column leads to a proportional decrease of the dilution factor resulting in a constant ratio of both. Beyond the matching point no dilution occurs and the dilution factor therefore has the value one.

Table II. Fixed Operating Conditions in the Optimization of GC in On-Line Combination with MS as Total Ion Current Detector

gas chromatograph	column temp	90 °C
	injection port temp	180 °C
	split ratio, β_S, for open tubular column	1:50
interface	temp	165 °C
	fixed gas flow rate into the ion source of the mass spectrometer	2.20 std cm³/min
mass spectrometer	electron energy for EI detector	24 eV
	electron emission current for EI detector	230 μA
	ion source temperature	170 °C
	ion source pressure	10^{-5} mbar

EXPERIMENTAL SECTION

Apparatus. A GC/MS system consisting of a dual-column gas chromatograph (Model 3700, Varian, Walnut Creek, CA) and a double focusing mass spectrometer (Model 112, Varian MAT, Bremen, F.R.G.) was used. The mass spectrometer was equipped with an electron impact ion source and a 600 L/s differential pump unit.

Both instruments were coupled on-line by an open interface according to Henneberg (*3*) consisting of a heated platinum capillary of 50 cm length and 0.15 mm i.d. which was connected via a narrow slit to the ion source inlet being a capillary of fixed dimension and temperature. The slit was flushed with helium.

The total ion current chromatograms were recorded on a potentiometric line recorder (Kompensograph III, Siemens AG, Karlsruhe, F.R.G.). The following chromatographic columns were used: packed columns made of stainless steel tubings of 1.5 m length and 1, 2, and 4 mm i.d.; glass capillary column of 23 m length and 0.3 mm i.d.

The operating conditions, except carrier gas and make-up gas flow rates, were kept constant during all experiments and are given in Table II.

For capillary columns and 1 mm i.d. packed columns the interface slit was flushed by a make-up gas for which helium was used. The make-up gas flow was adjusted by minimizing the background signal due to the entering of air into the ion source. The optimal make-up gas flow rate was found to be 130 cm³/min for capillary columns and 600 cm³/min for 1 mm i.d. packed columns measured at ambient temperature and atmospheric pressure.

Chemicals. In both types of gas chromatographic columns methyl silicone (OV 101, E. Merck, Darmstadt, F.R.G.) was used

as stationary liquid. The packed columns were filled with a packing consisting of a low surface area silica support (Volaspher A2, 100–125 μm, E. Merck) coated with 3% (g/g) of stationary liquid. The carrier gas was helium of 99.996% purity (Messer Griessheim, Düsseldorf, F.R.G.).

Four *n*-alkanes (nonane, decane, undecane, and dodecane) and two terpenes (β-pinene and camphor) were used as test compounds (from E. Merck and Fluka, Buchs, Switzerland). Solutions of different concentrations of these compounds in hexane were used as samples.

Procedures. The calibration functions were determined for each test compound on each column with solutions of at least four different concentrations, injecting a fixed volume of 1 μL. The response was measured at least 3-fold for each concentration. The linear regression data of the recorded peak height in millivolts and the injected sample size in nanograms were calculated.

The background noise was determined by measuring at least 30 equidistant points of the base line signal at maximum amplification of the EI detector. From these data the standard deviation, s_{yo}, of the background output signal, y_o, was calculated.

The magnitude of extracolumn peak broadening effects due to injector, interface, and detector were determined from the chromatograms in the usual way. The contribution, σ_{te}^2, of the extracolumn effects to the peak variance is given by the intersection obtained at the linear regression of the peak variances, σ_{ti}^2, and the square of the retention times, t_{Ri}^2, for different components, i.

RESULTS AND DISCUSSION

Dependence of Theoretical Plate Height on Cross Sectional Area. The dispersion of a sample component, i, within the chromatographic column is described by the theoretical plate height, H_i, which is given in gas chromatography for packed bed columns by the van Deemter equation (*15*)

$$H_i = 2\lambda d_p + \frac{2}{\tau}\frac{D_{mi}}{u} + \frac{8}{\pi^2}\frac{\kappa_i}{(1+\kappa_i)^2}\frac{d_f^2 u}{D_{si}} \qquad (12)$$

and for open tubular columns by the Golay equation (*16*)

$$H_i = 2\frac{D_{mi}}{u} + \frac{1}{24}\frac{1+6\kappa_i+11\kappa_i^2}{(1+\kappa_i)^2}\frac{r_0^2 u}{D_{mi}} + \frac{2}{3}\frac{\kappa_i}{(1+\kappa_i)^2}\frac{d_f^2 u}{D_{si}} \qquad (13)$$

with d_p = mean particle diameter, u = flow velocity of the mobile phase, D_{mi} = diffusion coefficient of component, i, in the mobile phase, m, D_{si} = diffusion coefficient of component, i, in the stationary phase, s, λ = factor characterizing the packing geometry, τ = tortuosity factor, κ_i = capacity factor = mass distribution coefficient, d_f = mean film thickness of the stationary liquid, and r_0 = inner radius of the open tubular column.

In the case of open tubular columns the interdependence of theoretical plate height and flow rate follows from eq 13 considering that the flow rate in the column, w_C, is given by

$$w_C = \pi r_o^2 u \qquad (14)$$

We see that the second term in eq 13 as well as the flow rate increase in proportion to the cross sectional area, πr_o^2.

In the theoretical plate height equation of packed bed columns two geometrical factors, τ and λ, occur. In a first look the theoretical plate height of this column type should not depend on the column diameter (cross sectional area). It is conceivable, however, that the packing geometry is influenced by the column diameter, d_C, which means that the packing factor, λ, could vary with d_C. Such an effect would result in a parallel shift of the H–u curve.

This prediction of the theory is not confirmed by our experimental results which are presented in Table III and Figure 3. As we can see not only are the H–u curves shifted parallel to lower values with decreasing column diameter but also the slope on the right hand side of the minimum decreases significantly, which causes also a shift of the minimum to higher flow velocities. This phenomena can be related to findings in high-pressure gas chromatography (*17*) which show that the van Deemter equation is a simplification of a more general equation which holds also for liquid chromatography. Furthermore, eq 12 and 13 describe only the situation at a given longitudinal position, z, of the column since the pressure drop causes a velocity gradient because of the compressibility of a gas. In practice the average theoretical plate height at the average flow velocity is measured. Because of the nonlinearity of the flow velocity gradient $u(z)$ and the function $H(u)$ the average values do not follow exactly eq 12 and 13 if the pressure drop is not negligible (*18*, *19*). The problem needs further investigation but is of minor importance for the topic of this paper. In a first approximation we can conclude, that the theoretical plate height at a given flow velocity decreases with decreasing column diameter. The small differences of the H–u curves of different compounds on a given column are the result of the combined effect of different values of the capacity factor and the diffusion coefficient. The crossing of the curves on a given column is caused by the differences of the diffusion coefficients.

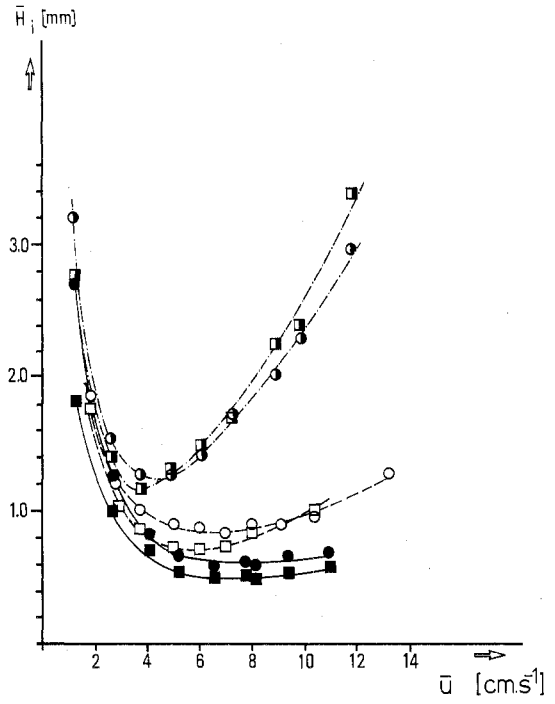

Figure 3. Plot of the average theoretical plate height, $\bar{H}_i$, as function of the mean flow velocity, $\bar{u}$, of the mobile phase for packed bed columns of different inner diameter: d_c = 4 mm (-·-), 2 mm (---), and 1 mm (—); compounds (◑, ○, ●) nonane (κ_i = 4.66, 4.58, and 5.17, respectively), (◨, □, ■) dodecane (κ_i = 36.0, 35.7, and 39.5).

For the detection limit of a GC/MS system the flow rate is the crucial parameter. Therefore it is more appropriate to consider the dependence of the theoretical plate height as a function of the flow rate at the column outlet. Such a plot is shown in Figure 4. We can see that both the open tubular and the 1 mm packed bed column have low H values at the fixed inlet flow rate of the mass spectrometer being 2.20 cm^3/min. The other two packed columns have significantly higher H values at this flow rate. It is obvious that only the first two columns should be used in order to achieve a low detection limit without loss in resolution.

Minimizing of the Detection Limit by Adjustment of the Column Cross Sectional Area. The sensitivity of a mass spectrometer depends on the ion production rate in the ion source which is determined for a given sample concentration

Table III. Chromatographic Characteristics of Columns with Different Cross Sectional Area[a]

column	mean flow velocity, $\bar{u}$ [cm s^{-1}]	theoretical plate height (H_i) for the following compounds					
		nonane	β-pinene	decane	undecane	camphor	dodecane
		capacity factor κ_i					
open tubular 0.3 mm × 23 m		0.63	1.17	1.26	2.52	3.55	4.97
	4.6	1.12	1.05	0.98	0.97	1.20	0.91
	10.4	0.50	0.53	0.45	0.44	0.55	
	21.4	0.31	0.31	0.31	0.31	0.32	0.30
	34.3	0.25	0.31	0.30	0.32	0.29	0.31
	46.7	0.27	0.27	0.27	0.31	0.32	0.36
	57.3	0.29	0.27	0.29	0.36	0.39	0.44
	73.3	0.29	0.33	0.41	0.46	0.41	0.54
	86.6	0.36	0.40	0.49	0.63	0.56	0.73
	97.7	0.49	0.55	0.53	0.75	0.68	0.89
		capacity factor κ_i					
packed bed 1 mm × 1.5 m		5.17	8.92	10.3	20.4	25.0	39.5
	1.3	2.74		2.38	2.23	2.80	1.82
	2.7	1.25	1.45	1.17	1.11	1.41	1.05
	4.1	0.84	0.91	0.77	0.72	0.92	0.70
	5.2	0.66	0.83	0.65	0.61	0.72	0.55
	6.6	0.58	0.61	0.56	0.54	0.62	0.51
	9.4	0.58	0.60	0.57	0.52	0.58	0.50
	10.9	0.59	0.79	0.62	0.58	0.60	0.56
		capacity factor κ_i					
packed bed 2 mm × 1.5 m		4.58	8.02	9.24	18.0	22.2	35.7
	1.9	1.73	2.18	1.68	1.61	2.04	1.50
	2.8	1.20	1.44	1.12	1.08	1.44	1.01
	3.8	1.00	1.12	0.93	0.86	1.05	0.84
	5.0	0.90	0.84	0.85	0.73	0.89	0.69
	6.0	0.87		0.73	0.66	0.80	0.69
	7.0	0.82	0.77	0.82	0.70	0.80	0.72
	8.0	0.88	0.77	0.76	0.72	0.81	0.86
	9.3	0.77	0.87	0.77	0.76		
	10.1	0.92	1.10	0.91	1.00	0.97	0.97
	13.0	1.25	1.46	1.45		1.09	1.45
		capacity factor κ_i					
packed bed 4 mm × 1.5 m		4.66	7.91	9.27	18.2	22.8	36.0
	1.3	3.20		2.96	2.79	3.24	2.73
	2.7	1.36	1.85	1.47	1.43	1.73	1.40
	3.7	1.27	1.38	1.23	1.22	1.28	1.15
	4.9	1.25	1.27	1.28	1.24	1.24	1.29
	6.1	1.41	1.24	1.35	1.47	1.35	1.49
	7.3	1.72	1.53	1.70	1.74	1.39	1.67
	8.9	2.05	2.02	2.08	2.14	1.93	2.23
	9.8	2.28	2.02	2.20	2.40	2.14	2.39
	11.8	2.95	3.05	3.48	3.24	2.81	3.38

[a] The determination of the extracolumn contribution to the peak variance by linear regression of the peak variances and the squares of the retention times of the six test compounds led to the result that the extracolumn contribution was not significant with all four types of columns.

by the inlet flow rate. The inlet flow rate influences the sensitivity since it determines the mass flow of the sample to the ion source as well as the pressure in the ion source. Depending on the pumping rate and the ion source design, an optimum inlet flow rate exists for which the sensitivity is a maximum. In general this optimum inlet flow rate is fixed by means of an inlet tubing having the corresponding flow resistance.

The mass sensitivity of a GC/MS system with open direct coupling interface depends on the ratio between the inlet flow rate of the ion source of the mass spectrometer on the one hand and the outlet flow rate of the chromatographic column on the other hand. Only if the outlet flow rate of the column is the same as the inlet flow rate of the ion source and no split occurs at the interface, the total sample is transferred from the gas chromatograph to the mass spectrometer. If the column outlet flow rate is larger than the inlet flow rate of the mass spectrometer, a part of the sample is split off at the interface and is not used for measurement in the mass spectrometer; if the outlet flow rate of the column is smaller than the inlet flow rate of the mass spectrometer, the sample is diluted by make-up gas. In such a case the mass flow of sample to the ion source is reduced compared to the case of exactly matched flow rates if the sample concentration in the chromatographic effluents is the same.

In principle we have two ways to adjust the column outlet flow rate: via the flow velocity and via the cross sectional area of the column. It is well-known and theoretically understood that the column efficiency depends on the flow velocity having a maximum value at a given flow velocity. In the previous

Table IV. Detection Limits of GC/MS Systems with Columns of Different Cross Sectional Area

test compd	column outlet flow rate (w_{CL}), cm^3 min^{-1}	$[\kappa_i/(1+\kappa_i)]N_i^{1/2}$	sensitivity (S_i), mV ng^{-1}	rel std dev of sensitivity, ±%	linearity (r^2)[a]	base line noise (s_{yo}), mV	detection limit ($Q_{i\,min}$),[b] ng	$F_{opt} \times 10^2$, mm^{-3}
Wall Coated Open Tubular Column 0.3 mm × 23 m								
nonane	0.44	83.0	3.54	5.8	0.9943	9.7	8.2	2.4
	1.45	116.5	12.8	2.8	0.9986	7.0	1.6	17.5
	2.42	109.7	10.7	3.5	0.9949	7.9	2.2	23.5
	4.13	84.1	8.79	9.1	0.9966	3.7	1.3	13.8
β-pinene	0.44	112.0	2.30	4.9	0.9953	9.7	12.7	2.6
	1.45	146.8	6.45	3.1	0.9981	7.0	3.2	15.1
	2.42	157.0	5.65	5.4	0.9942	7.9	4.2	26.0
	4.13	110.4	3.77	3.6	0.9962	3.7	2.9	12.9
decane	0.44	126.4	2.91	7.3	0.9896	9.7	10.0	3.1
	1.45	153.5	9.67	3.6	0.9974	7.0	2.2	15.3
	2.42	158.2	7.76	3.5	0.9964	7.9	3.0	24.4
	4.13	116.3	5.71	8.2	0.9867	3.7	1.9	13.2
undecane	0.44	164.1	1.68	6.9	0.9906	9.7	17.3	2.6
	1.45	191.1	5.64	4.3	0.9964	7.0	3.7	11.8
	2.42	182.3	4.54	5.2	0.9919	7.9	5.2	16.2
	4.13	125.2	2.92	7.2	0.9900	3.7	3.8	7.6
camphor	0.44	159.5	0.91	6.9	0.9903	9.7	31.9	1.8
	1.45	219.7	2.29	5.5	0.9940	7.0	9.1	11.0
	2.42	190.4	1.80	3.1	0.9982	7.9	13.1	12.5
	4.13	142.1	1.36	5.1	0.9923	3.7	8.1	7.1
dodecane	0.44		0.95	8.2	0.9867	9.7	30.6	
	1.45	228.0	2.92	3.2	0.9980	7.0	7.2	8.5
	2.42	190.2	2.29	7.9	0.9815	7.9	10.3	7.4
	4.13	133.8	1.31	5.2	0.9947	3.7	8.4	4.4
Packed Bed Column 1 mm × 1.5 m								
nonane	0.8	29.1	19.6	4.3	0.9963	2.4	0.370	7.3
	2.7	40.0	70.4	5.7	0.9963	2.0	0.085	38.6
	7.9	39.2	37.3	5.1	0.9949	3.2	0.260	36.9
β-pinene	0.8	28.9	7.14	6.2	0.9921	2.4	1.01	4.2
	2.7	38.3	36.6	2.9	0.9984	2.0	0.160	20.5
	7.9	39.2	19.9	4.7	0.9957	3.2	0.480	21.6
decane	0.8	32.5	13.5	5.5	0.9940	2.4	0.530	4.7
	2.7	43.6	41.9	4.8	0.9955	2.0	0.140	23.3
	7.9	44.9	22.5	5.0	0.9950	3.2	0.430	24.4
undecane	0.8	34.9	8.45	2.7	0.9986	2.4	0.860	2.7
	2.7	47.3	24.1	5.9	0.9931	2.0	0.250	13.7
	7.9	48.2	11.1	4.0	0.9968	3.2	0.870	14.4
camphor	0.8	31.3	3.40	17.9	0.9388	2.4	2.13	1.8
	2.7	43.8	12.1	3.5	0.9977	2.0	0.490	9.6
	7.9	47.9	6.70	4.7	0.9956	3.2	1.44	11.6
dodecane	0.8	37.2	4.53	0.93	0.9998	2.4	1.60	1.6
	2.7	51.0	12.6	5.8	0.9933	2.0	0.480	8.2
	7.9	50.9	5.92	4.8	0.9957	3.2	1.63	8.1
Packed Bed Column 2 mm × 1.5 m								
nonane	5.5	29.0	10.2	6.3	0.9920	2.6	0.770	5.7
	17.5	34.1	11.1	2.7	0.9986	3.0	0.820	7.9
	28.0	33.8	7.17	10.3	0.9793	1.2	0.520	7.8
	55.0	28.4	5.08	2.6	0.9986	0.9	0.510	5.5
β-pinene	5.5	28.7	5.87	7.2	0.9895	2.6	1.34	3.2
	17.5	34.3	6.22	3.6	0.9975	3.0	1.47	4.6
	28.0	39.2	4.64	8.7	0.9852	1.2	0.800	6.0
	55.0	28.5	3.16	2.1	0.9991	0.9	0.830	3.2
decane	5.5	32.9	6.33	5.4	0.9936	2.6	1.24	3.7
	17.5	40.9	6.85	3.1	0.9980	3.0	1.33	5.7
	28.0	39.9	4.71	11.1	0.9758	1.2	0.780	5.4
	55.0	28.9	3.05	3.0	0.9983	0.9	0.860	2.8
undecane	5.5	35.4	3.54	2.8	0.9985	2.6	2.22	2.2
	17.5	45.5	3.91	4.4	0.9961	3.0	2.33	3.6
	28.0	43.3	2.15	1.3	0.9997	1.2	1.71	3.3
	55.0	36.9	1.73	8.8	0.9850	0.9	1.51	2.4
camphor	5.5	31.0	2.30	4.6	0.9958	2.6	3.42	1.3
	17.5	41.6	2.51	3.9	0.9970	3.0	3.64	2.4
	28.0	41.5	1.44	8.6	0.9863	1.2	2.57	2.4
	55.0	35.6	1.13	11.1	0.9762	0.9	2.30	1.8

Table IV (*Continued*)

test compd	column outlet flow rate (w_{CL}), cm^3 min^{-1}	$[\kappa_i/(1+\kappa_i)]N_i^{1/2}$	sensitivity (S_i), mV ng^{-1}	rel std dev of sensitivity, ±%	linearity (r^2)[a]	base line noise (s_{yo}), mV	detection limit ($Q_{i\,min}$),[b] ng	$F_{opt} \times 10^2$, mm^{-3}
dodecane	5.5	36.5	1.75	1.4	0.9996	2.6	4.48	1.2
	17.5	45.1	2.02	3.0	0.9983	3.0	4.53	1.8
	28.0	40.6	1.05	10.8	0.9978	1.2	3.50	1.4
	55.0	31.2	0.66	6.7	0.9912	0.9	3.96	0.9
			Packed Bed Column 4 mm × 1.5 m					
nonane	6.0	18.1	2.22	1.4	0.9996	7.3	9.8	0.53
	30.0	28.9	2.84	5.6	0.9937	3.1	3.2	1.4
	82.0	24.7	2.39	1.6	0.9995	1.6	2.0	0.99
	224.0	18.9	1.16	0.3	1.0000	1.1	2.7	0.58
β-pinene	6.0	17.8	0.791	4.8	0.9954	7.3	27.5	0.31
	30.0	31.2	1.26	2.1	0.9991	3.1	7.3	0.92
	82.0	28.4	1.10	2.2	0.9990	1.6	4.5	0.76
	224.0	20.1	0.512	2.0	0.9993	1.1	6.2	0.38
decane	6.0	20.7	1.43	7.5	0.9889	7.3	15.2	0.34
	30.0	31.5	1.75	3.5	0.9975	3.1	5.2	0.80
	82.0	27.3	1.50	1.8	0.9994	1.6	3.3	0.61
	224.0	19.1	0.69	0.3	0.9999	1.1	4.6	0.30
undecane	6.0	22.4	0.833	0.5	0.9999	7.3	26.1	0.21
	30.0	33.7	0.968	4.7	0.9957	3.1	9.5	0.47
	82.0	28.4	0.752	1.9	0.9993	1.6	6.5	0.33
	224.0	20.8	0.323	0.6	0.9999	1.1	9.8	0.18
camphor	6.0	21.0	0.294	3.8	0.9973	7.3	74.0	0.15
	30.0	34.0	0.402	2.3	0.9968	3.1	22.8	0.38
	82.0	32.2	0.328	2.2	0.9991	1.6	14.9	0.34
	224.0	22.7	0.152	1.3	0.9998	1.1	20.8	0.17
dodecane	6.0	23.2	0.453	3.1	0.9980	7.3	48.0	0.11
	30.0	33.7	0.507	2.8	0.9984	3.1	18.0	0.24
	82.0	29.7	0.364	2.8	0.9986	1.6	13.4	0.18
	224.0	20.9	0.148	2.7	0.9989	1.1	21.4	0.091

[a] r = correlation coefficient of linear regression. [b] $Q_{i\,min} = 3(s_{yo}/S_i)$ = detection limit defined as mass of component i corresponding to three times the standard deviation of the base line.

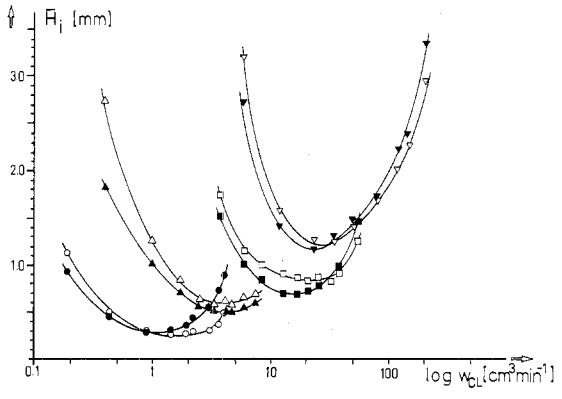

Figure 4. Plot of the average theoretical plate height, $\bar{H}_i$, as function of the flow rate, w_{CL}, of the mobile phase at the column outlet for packed bed columns of different inner diameters: d_C = 1 mm (△ ▲), 2 mm (□, ■), and 4 mm (▽ ▼), and an open tubular column (○ ●); compounds, nonane (○ △ □ ▽) and dodecane (● ▲ ■ ▼). κ values for packed bed columns are as in Figure 3, for open tubular column 0.63 and 4.97, respectively.

section we have seen that the column efficiency depends on the cross sectional area of the column not only for open tubular columns but also for packed bed columns. Equation 2 describes how the chromatographic resolution is influenced by the column efficiency which is defined by the theoretical plate number, $N_i = L/H_i$. Therefore we have to conclude that both means to influence the column outlet flow rate affect also the separation. The maximum sensitivity and minimum detection limit can be expected if the column is operated at the flow velocity giving the minimum theoretical plate height and a cross sectional area is used which matches the outlet flow rate of the chromatograph to the fixed inlet flow rate of the mass spectrometer.

In Table IV the experimental detection limits of GC/MS systems with chromatographic columns of different cross sectional area operated at different flow rates are shown. Since the column efficiencies and capacity factors are not the same, especially the open tubular column has more than an order of magnitude larger column efficiencies and significant lower capacity factors, the optimization factor, F_{opt}, defined by eq 11, is the appropriate measure to compare the different systems. It can be seen that the open tubular column and the packed bed column with 1 mm diameter have about the same F_{opt} values. In the interpretation of these results it has to be taken into account that the open tubular column was operated with split injection. With splitless injection the open tubular column would be superior due to its smaller cross sectional area. The effect of the smaller cross sectional area is about compensated, however, in the split injection mode by the chosen split ratio, β_S.

From Table IV we can further see that the mass sensitivity of the GC/MS systems increases with the flow rate of the column effluent up to a value corresponding to about the fixed inlet flow rate of the mass spectrometer, above that it decreases again. The change of mass sensitivity in Table IV, however, does not follow exactly the sensitivity change predicted by eq 9 which can be applied for GC/MS systems with fixed inlet flow rate of the mass spectrometer for which the sensitivity is proportional to the inlet concentration of the mass spectrometer. The experimental deviation from the prediction of eq 9 could be caused by some dilution at the interface occurring also at and above the flow matching point. A modification of the interface design allowing a more exact

lining of the chromatographic outlet and the mass spectrometric inlet tubing should reduce this unwanted additional dilution by the make-up gas.

Table IV shows also that the base line noise at low flow rate is generally somewhat higher, especially in the case of the open tubular column. This result is probably caused by a not sufficient depression of the air diffusion into the ion source of the mass spectrometer by the scavenge flow of helium. A decrease of the noise level of one-third to one-tenth of the present values seems to be possible if the interface is designed in such a way that the air diffusion into the ion source is avoided more effectively.

ACKNOWLEDGMENT

The assistance of B. Goose in writing the paper is appreciated.

LITERATURE CITED

(1) Holmes, J. C.; Morell, F. A. *Appl. Spectrosc.* **1957**, *11*, 86.
(2) Gohlke, R. S. *Anal. Chem.* **1959**, 31, 535.
(3) Henneberg, D. *Z. Anal. Chem.* **1961**, *183*, 12.
(4) Watson, J. T.; Biemann, K. *Anal. Chem.* **1964**, *36*, 1135.
(5) Rhyhage, R. *Anal. Chem.* **1964**, *36*, 759.
(6) Grotch, S. L. *Anal. Chem.* **1970**, *42*, 1214.
(7) McFadden, William H. *J. Chromatogr. Sci.* **1980**, *18*, 97.
(8) Kenndler, Ernst; Schmid, Erich R. "Instrumentation for High-Performance Liquid Chromatography"; Huber, J. F. K., Ed.; Elsevier: Amsterdam, Oxford, New York, 1978; Vol. 13, pp 163–177.
(9) Ten Noever de Brauw, M. C. *J. Chromatogr.* **1979**, *165*, 207–233.
(10) *J. Chromatogr. Sci.* **1979**, *17*, 1–112; special issue "Gas Chromatography–Mass Spectrometry".
(11) Huber, J. F. K. *Z. Anal. Chem.* **1975**, *277*, 341.
(12) Huber, J. F. K. *Chimia Suppl.* **1970**, 24.
(13) Huber, J. F. K.; Hulsman, J. A. R. J. *Anal. Chim. Acta* **1967**, *38*, 305.
(14) Huber, J. F. K.; Hulsman, J. A. R. J.; Meijers, C. A. M. *J. Chromatogr.* **1971**, *62*, 79.
(15) van Deemter, J. J.; Zuiderweg, F. J.; Klinkenberg, A. *Chem. Eng. Sci.* **1956**, *5*, 271.
(16) Golay, M. In "Gas Chromatography, 1958"; Desty, D. H., Ed., Butterworth: London, 1958; p 36.
(17) Huber, J. F. K.; Lauer, H. H.; Poppe, H. *J. Chromatogr.* **1975**, *112*, 377.
(18) Giddings, Calvin; Seager, Spencer L.; Stucki, Larry R.; Stewart, Georg H. *Anal. Chem.* **1960**, *32*, 867–870.
(19) Sternberg, J. C.; Poulson, R. E. *Anal. Chem.* **1964**, *36*, 58–63.

RECEIVED for review October 20, 1981. Resubmitted April 5, 1982. Accepted April 5, 1982. The paper was presented at the 6th International Symposium "Advances and Application of Chromatography in Industry", Bratislava, Sept 16–19, 1980. We wish to express our gratitude to the SEA Foundation for financial support of the project.

Identification of Crude Oils by Selective Chemical Ionization Mass Spectrometry[1]

P. Burke and K. R. Jennings*

Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL, England

R. P. Morgan* and C. A. Gilchrist

Shell Research Limited, Thornton Research Centre, P.O. Box 1, Chester, England

OH^- chemical ionization has been used to ionize selectively a series of crude oils. The results show that this method can provide positive identification of the geographical area of origin of an oil and in the majority of cases can identify the individual fields.

One of the problems of electron impact mass spectrometry is that a gross mixture of 100–200 compounds can yield as many as 5000 significant (intensity >0.1% of the largest peak) ionic species. Thus, much time must be spent on interpretation when a total analysis is required. Use of a soft ionization process such as field desorption (FD) (*1*) or chemical ionization (CI) (*2*) can reduce the number of ionic species formed, by reducing the amount of energy imparted to the ions during the ionization process. Recently, further simplification of spectra has been demonstrated under CI conditions by using special reagent gases which selectively ionize only certain types of molecules. By use of this latter technique, a method has been developed that should provide a fast and efficient method for the identification of crude oils.

Analysis of Crude Oils. Considerable effort has been devoted to the characterization and identification of crude oils by environmental protection agencies and the petroleum industry. Unfortunately no single technique exists which is sufficient for crude oil identification and hence a number of complementary methods have to be used. These methods primarily include (i) low resolution gas chromatography (*3–6*), (ii) neutron activation (*7*), (iii) X-ray fluorescence spectroscopy, (iv) sulfur-print gas chromatography (*8*), (v) infrared spectroscopy in the 2–15 μm range (*9, 10*), (vi) ^{13}C nuclear magnetic resonance spectroscopy (*11*), (vii) gas chromatography selective ion monitoring (*12–14*).

What is required is a simple and rapid method of crude oil identification which can be used to identify a spilled oil from a short list of possible candidates.

The various processes involved in weathering deplete the classes of hydrocarbons present in oils at different rates. Of the four main weathering processes that of biological degradation is known, for example, to deplete *n*-alkanes at a faster rate than branched alkanes (*15*).

The different physical properties of various hydrocarbon classes (boiling points, aqueous solubilities, etc.) are reflected in the differential rates of depletion by the other main weathering processes of evaporation (the most rapid and largest bulk effect) (*16*), solution, and photolysis.

What is desirable, therefore, in addition to the above mentioned rapidity and ease of data analysis, is a technique that observes as few compound classes as possible, in order to reduce the interference of competing weathering processes, whilst retaining sufficient diagnostic power for crude oil identification.

OH^- Chemical Ionization (CI). An ionization technique which would yield molecular ion profiles will have potentially

[1] This paper is dedicated to the memory of Geoff Steel who tragically died March 29, 1980, and who initiated and inspired this work.

0003-2700/82/0354-1304$01.25/0