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Gas chromatography as an industrial process operation—application to essential oils

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Chromatography is a separation process long used at the laboratory scale. It is based on partition or adsorption equilibria. It uses a fixed bed, usually a column packed with small particles of an adsorbent or an inert support coated with 5-20% of a suitable nonvolatile liquid. A mobile phase (a gas in gas chromatography) percolates through the fixed bed and carries along a plug of the mixture. Each component of the mixture undergoes equilibrium with the stationary phase and appears at the column exit as a band of a certain width, depending on the column parameters, at a time which is a function of the equilibrium constant. The components of the mixture are diluted in the mobile phase and more or less separated from each other.

Chromatographic techniques are thus preparative in nature. Although in analytical applications the eluent is discarded after its composition is measured, it is in principle a simple operation to direct the separate zones to vessels where they can be recovered. Many theoretical, experimental, and technological problems arise, however, which have plagued the various teams who have tried to turn gas chromatography into an industrial separation process. We have solved these problems and present here results obtained with various pilot and demonstration units, working reliably for extended periods of time during the last years, unattended overnight, with production capacities between 2 and 15 t/year for those using 125 mm i.d. columns and 10 times larger for those using a 400 mm i.d. column.

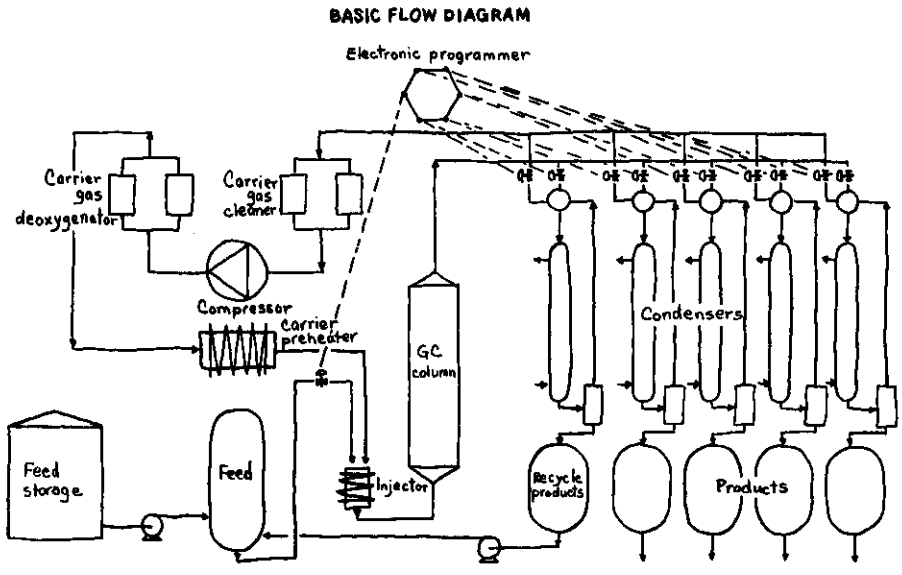

Figure 1

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Experimental

A scheme of a typical unit is given in figure 1 and a photograph of one of the units currently in operation in figure 2. The main features are the feedstock injection system, the column, the condensers-receivers and the control unit. Helium, or better, hydrogen, is used as carrier gas for maximum production. This gas is recycled after purification on charcoal. A compressor permits operation under reduced outlet pressure when necessary.

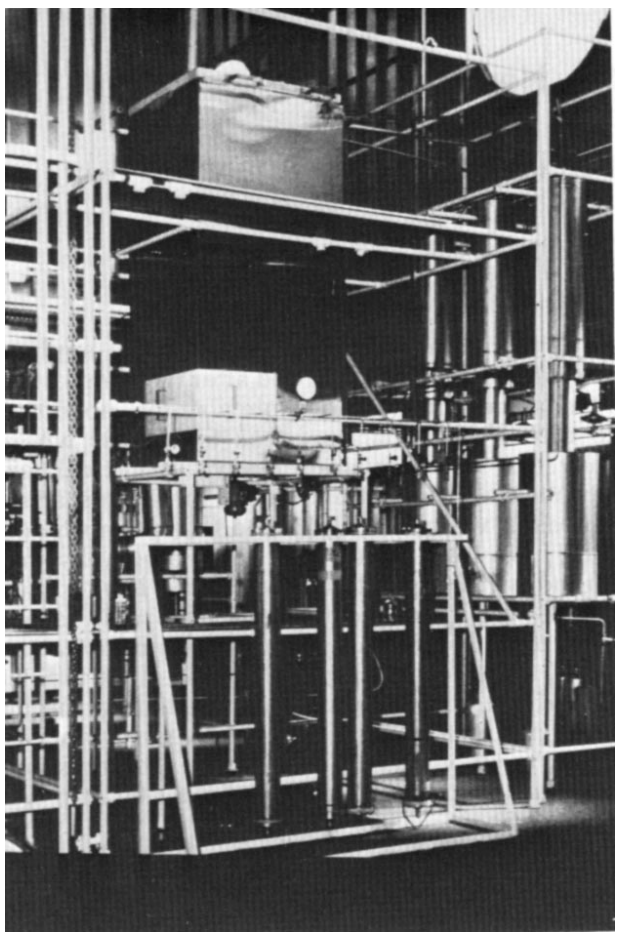

Figure 2. Industrial prep-scale gas chromatography.

A vaporizer permits the injection of a constant mass-flow of feedstock vapor into the column for repetitive periods of time. Typically 10 to 150 g are injected during a period of from 10 to 30 sec; on a cycle from a few to 30 minutes apart, on 125 mm i.d. columns.

The column is packed with fine particles of narrow size distribution of an inert support specially treated to suppress or reduce the catalytic effects which might provoke decomposition, isomerization, or polymerization. A nonvolatile liquid—we developed special phases, polar and nonpolar, stable up to temperatures between 200 and 300°C—is coated on the support (density of liquid 0.1 to 0.2 kg/dm^3). A proprietary packing technology, involving vibrations and shocks of carefully controlled intensity, permits homogeneous packing, resulting in high column efficiency. The same efficiency—800 to 100 plates per meter—is achieved for columns 125 to 400 mm i.d.

Condenser-receivers collect the separated zones at column outlet. The careful design of these heat exchangers, which always work in transitory conditions, permits excellent recovery yields, in excess of 97%.

A control unit actuates the valves and energy sources of the vaporizer and the condenser/receivers. It is based on time. This is made possible by the excellent control of pressures and temperatures, allowing a reproducibility of retention times better than 0.1% over extended periods of time. Time control permits easy, fast start-ups of new production, the collection of pure products from apparently nonresolved bands, and flexibility in the definition of the end products—pure compounds, intermediate fractions, elimination of one component of a mixture, and extraction of non-detected impurities. This system has been very reliable.

Theoretical

All attempts at deriving a model of finite concentration chromatography from the general theory of analytical chromatography have failed because large solute concentrations result in peak broadening much more important than diffusion and resistance to mass-transfer which are important at low concentrations. Even change of peak profile with growing asymmetry occurs when sample size becomes large.

Among the many effects of large concentration, two are of major importance and should be accounted for in priority: the sorption and the isotherm effects. The first of these is due to the fact that a given mass of compound occupies a much larger space in the gas phase than in solution. As the mass-flow rate of carrier gas is kept constant, the gas velocity is larger inside a solute band than upstream or downstream. The larger the concentration, the larger the velocity, with

the consequence that the part of the band where concentration is maximum tends to overrun the others and a steep front appears.

At large concentrations, partition isotherms are no longer linear. The plot of amount of solute dissolved in a given quantity of stationary phase versus partial pressure is convex towards the pressure axis, which means that solubility increases with increasing partial pressure, and the velocity of the part of the band where concentration is larger becomes the lowest; a steep tail occurs.

These two effects are opposite. The isotherm effect prevails at low temperature where vapor pressure is low and solubility large, while the sorption effect dominates at high temperature. Valentin has shown that the two effects cancel each other in a temperature range which is such that the solute vapor pressure is equal to a column average pressure. As there is an optimum gas velocity and a relationship between gas velocity and inlet and outlet pressures, the Valentin condition permits the selection of optimum column temperature or of optimum outlet pressure if the temperature is determined by the thermal stability of the compounds prepared or the stationary phase.

The determination of the mass-balance equations of solutes and carrier gas permits the numerical calculation of peak profiles. The broadening effect of resistances to mass-transfer may be accounted for by the use of an empirical apparent diffusion coefficient. One of the major properties of the set of partial differential equations obtained, which results from the fact that they are not linear, is the possibility that stable concentration discontinuities propagate along the column. This explains quantitatively the occurrence of very steep fronts or tails on band profiles obtained in case of large column overloading (cf. fig. 3). Such calculations are used to optimize the design and operating parameters of columns.

Results and discussion

Figures 3 through 6 show results obtained in various separation problems which are related to essential oils: separation of two closely related isomers (fig. 3: trans-trans and trans-cis farnesols), extraction of the two main components from a complex mixture (fig. 4: extraction of humulene and beta-caryophyllene from clove essential oil), extraction of one component out of a complex mixture (fig. 5: limonene out of an es-

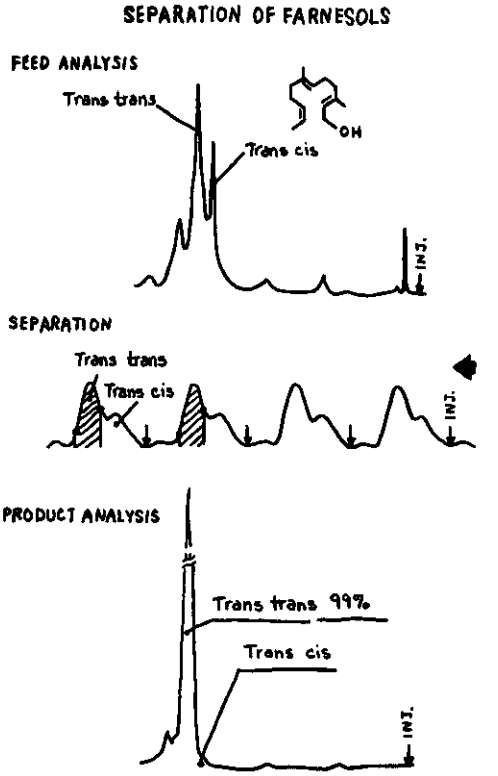

Figure 3. Feed analysis: Column 3 m length, Chromosorb P coated with 20% Carbowax 20 M, temperature 170°C, Helium carrier gas. 1st stage operation: Column 40 mm i.d., 2 m length, Chromosorb P coated with 20% Carbowax 20 M, temperature 180°C, Hydrogen carrier gas, cycle time 15.3 min, feedrate 12 milliliters per cycle. 2nd stage operation: Column 40 mm i.d., 4 m length, Chromosorb P coated with 20% Carbowax 20 M, temperature 170°C, Hydrogen carrier gas, cycle time 12 min, feedrate 8 milliliters per cycle. Product analysis: same conditions as under "Feed analysis." Purity 99.9%.

sential oil of orange), separation of a complex mixture in two fractions (fig. 6: deterpenation of lemon oil). These results illustrate the selectivity of the process. Through proper selection of a convenient stationary phase, it is possible to extract a compound present at small concentration, or to eliminate impurities.

Other characteristics of the process are illustrated by these figures. The interest of a multistep scheme for processing complex mixtures with heavy components (cf. fig. 5), the possibility of extracting compounds at a rather high degree of purity from unresolved or hardly resolved bands (cf. fig. 4 and 5). It is also observed that, in agreement with theoretical prediction,

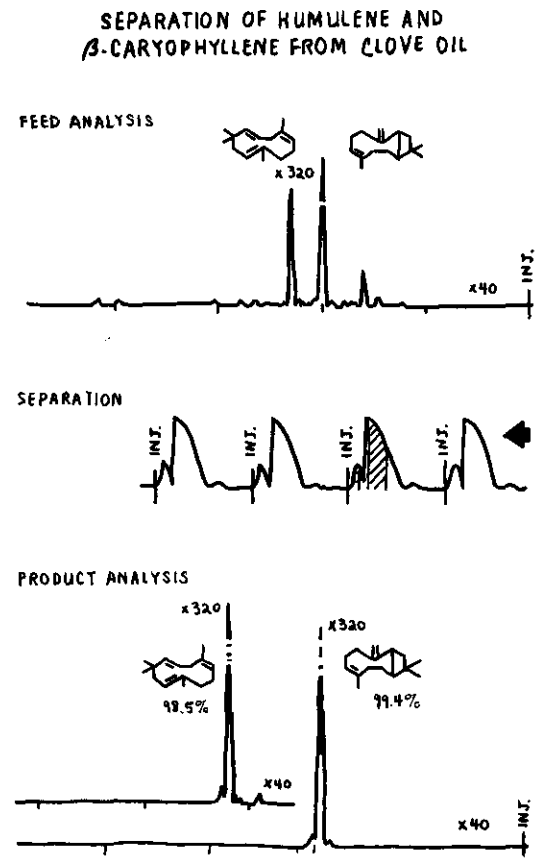

Figure 4. Feed analysis: Capillary column 92 m length coated with Carbowax 20 M, temperature programmed from 130-180°C at 2°C/min, Helium carrier gas, 2.9 milliliters/min. Separation: Column 40 mm i.d., 3 m length, 20% Carbowax 20 M on Chromosorb P, temperature 170°C, Helium carrier gas, 3 liters/min, feedrate 5 milliliters per cycle. Product analysis: Same conditions as under "Feed analysis." Purity: humulene 98.5%, caryophyllene 99.4%.

Figure 5. Feed analysis: Column 3 m length, Chromosorb P coated with 20% Carbowax 20 M, temperature 170°C, Helium carrier gas. 1st stage operation: Column 40 mm i.d., 2 m length, Chromosorb P coated with 20% Carbowax 20 M, temperature 180°C, Hydrogen carrier gas, cycle time 15.3 min, feedrate 12 milliliters per cycle. 2nd stage operation: Column 40 mm i.d., 4 m length, Chromosorb P coated with 20% Carbowax 20 M, temperature 170°C, Hydrogen carrier gas, cycle time 12 min, feedrate 8 milliliters per cycle. Product analysis: Same conditions as under "Feed analysis." Purity 99.9%.

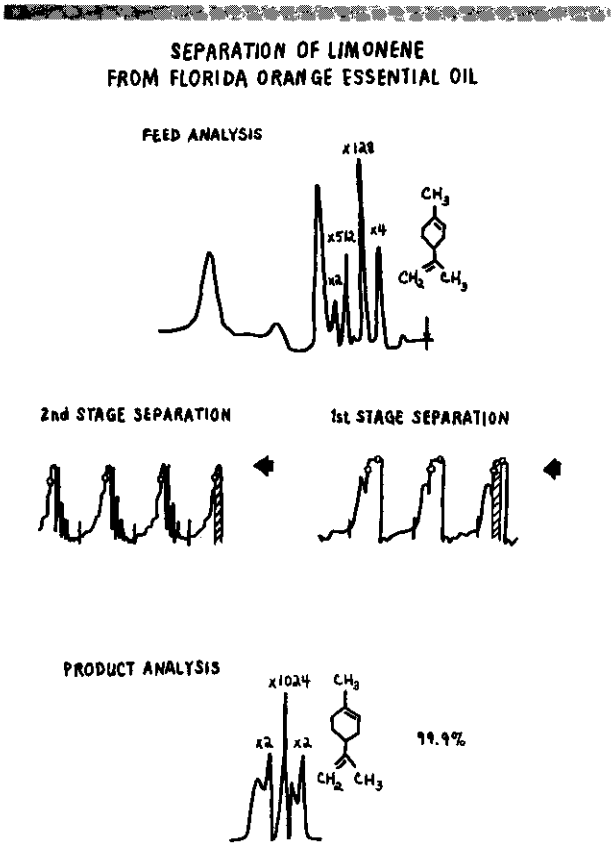

Figure 5

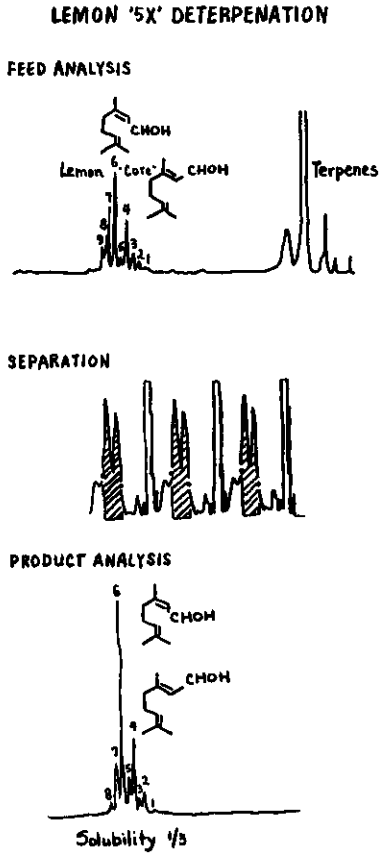

Figure 6. Separation: Column 40 mm i.d., 0.5 m length, Chromosorb coated with 20% ELF-SRTI polar stationary phase, temperature 150°C, inlet pressure: atmospheric. Product analysis: lemon core soluble in 2 to 3 of 70% EtOH.

Table I. Examples of chromatographic separations carried out on the demonstration unit

	CONCENTRATION Feedstock %	Product %	OPERATING CONDITIONS	PRODUCTION kg/h	OBSERVATIONS
Case No 1					
Pentane	99.300	99.995	Carrier gas: helium	1.5	The maximum purity was desirable.
Iso pentane	0.700	50 ppm	Temperature: 225°C		
			Outlet pressure atmospheric		
Case No 2					
Benzyl alcohol	99.5	99.6	Carrier gas: hydrogen	1	Example of selective removal of an impurity - short contact time (under reduced pressure) and the passification of the support prevents the degradation of the alcohol to the aldehyde.
Benzyl aldehyde	0.1		Temperature: 150°C		
Other compounds	0.4		Outlet pressure: 50 torr		
			Passified support		
Case No 3					
Alpha pinene	70	99 2	Carrier gas: hydrogen	2.5	Example of the simultaneous purification of two products.
Beta pinene	30	1 98	Temperature: 160°C		
			Outlet pressure atmospheric		
Case No 4					
Clove essential oil			Carrier gas: helium	0.4	Recovery of a purified product from a natural essential oil. The quality of the product is unimpaired in spite of the rather severe processing conditions (220°C)
Eugenol	75	99.8	Temperature: 160°C		
			Outlet pressure atmospheric		

the column length need not be long; 1 to 3 m is convenient in most cases. Large amounts of feedstock can be injected, but the concentration at injection should not be too large, otherwise the column could be flooded by the solution of mixture in stationary phase.

The separation shown in figure 7 illustrates the ability to work with a reduced outlet pressure if, because of problems of thermal stability of sample or stationary phase, it is the only way to fulfill the Valentin condition.

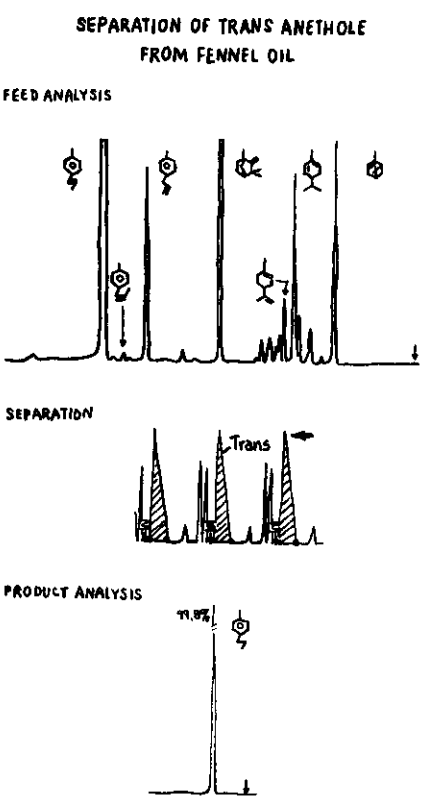

Figure 7. Feed analysis: Column 8 ft length, ⅛", Chromosorb WAW filling 5% Carbowax 20 M, Nitrogen 30 ml/mn, temperature 160°C, 0.1 µl. Separation: Column 40 mm i.d., 1 m length, Chromosorb G. NAW filling 4% FFAP, temperature 120°C, absolute pressure 1205 torr, 130 torr out, Helium carrier gas, cycle time 8 min, feedrate 0.8 gm/cycle.

Separations carried out with 40 mm i.d. columns have not been optimized carefully as it would not have been economic. Table I shows data for 4 separations which have been better optimized, using 125 mm i.d. columns. Production of large amounts of these compounds and of many others, which have to be kept confidential, has been carried out with our units. Throughputs between 3 and 20 tons per year and yields between 75 and 100% have been achieved depending on difficulty of the separation and its economics. There is a loss of no more than 2-3%. The unseparated fraction can be recycled.

Chromatography now belongs to the group of industrial processes of separation. This is proven by its successful application to many mixtures, including high boiling and thermolabile compounds. The process is easy and rapid to start up. The hold-up is negligible as well as the losses. Batch operations are much less costly than for distillation. Chromatography compares successfully with distillation when the relative volatility is less than 1.1 to 1.2, for azeotropic, pseudoazeotropic mixtures or those with pinched isotherms, for thermolabile compounds as the residence time is shorter, and to extract selectively one or a few compounds from complex mixtures, whether valuable or unwanted.

This process makes possible a significant reduction in processing costs for many specialty chemicals and intermediates as well as the production of new compounds.

Acknowledgment

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