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title
A CONCEPT FOR A MINIATURE GAS CHROMATOGRAPH

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A CONCEPT FOR A MINIATURE GAS CHROMATOGRAPH*

1.0 INTRODUCTION

Gas chromatographs have proven to be a reliable method for gas specie identification with detection sensitivity approaching as high as several parts per million. Based upon the mechanism of physical adsorption and desorption, an impulse of gas injected into the chromatograph column separates in time the gas components. The specie is identified by the delay time (or retention time) with respect to the initial impulse of gas. The shorter conventional columns are typically 1/2 m in length and a few millimeters in diameter backfilled with granulated particles. The associated hardware including the gas sample injector, valves, plumbing, furnace, detector, and electronics for a conventional gas chromatograph occupies a volume of several thousand cm³.

The concept of a miniature gas chromatograph having a size, for example, similar to the HP-35 mini-calculator should have a wide appeal for numerous applications, especially, if the cost per unit can be kept below \$1,000.

Some of the likely applications would be the following:

- Toxic gas monitors - gas sniffing in various industries, submarines, airplanes, mines, tunnels, and residential homes.
- Pollution detectors - exhaust stacks in various industries, surveillance equipment, and in auto garages for exhaust emission standards maintenance.
- Reaction gas analysis - for in-situ monitoring of gaseous products in experiments, for example, for in-situ coal gasification and oil shale retorting.

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- Law enforcement usage - for alcohol and narcotics detection.
- Security requirements for our nation.

It is envisioned the gas chromatograph can be reduced eventually to the size of a wristwatch for specific gas component identification.

The basic chromatograph consists of three main components; 1) the gas sample injector, 2) the column, and 3) the detector at the outlet. Generally the detection resolution determines the column length. The trade-off between the granulated particle size and the square root of the column length allows for the miniaturization of the chromatograph for a fixed resolution. Because of the short retention time in the reduced column length a fast gas sample injector is required. Methods are available that will allow a few millisecond gate period for sample injection. Micro-electronics technology can be used for 1) engraving the column channel onto a Si chip, and 2) the porous backfilling of the channel with chemical vapor deposition techniques. A miniature high-field gas ionizer and the ion-collector system can be integrated to the column. The detector signal is amplified and processed to the desired output format by an integrated circuit (IC) chip that is hybridized to the chromatograph.

The very small size of the column is amenable for rapid and uniform temperature cycling with a very small expenditure in the required electrical power. Also, the gas chromatograph can be utilized in severe 500°C - 700°C environments by incorporating high temperature electronic components at the detector output.

2.0 CHROMATOGRAPHY PRINCIPLES

Chromatography is a method for separating volatile components in the gas phase. The component is distributed between two phases, one named a mobile phase and the other the stationary phase. The mobile phase is transported by a carrier gas in a capillary column, and the stationary phase is adsorbed into a solid from the flowing mobile phase. Chromatography is based upon the kinetics of the adsorption-desorption process in the gas-solid interface in the column. In conventional chromatography two types of columns are used,

1) the open capillary column, and 2) the packed column. In the former the chromatograph column consists of a clear channel tube of about 300 μm in diameter and 100 m in length, and the latter consists of a column backfilled with granular particles ($\sim 200 \mu\text{m}$ in diameter) and a column length of about 1 m.

The gas velocity in the column is given by

$$v = \frac{-K_o}{\eta f} \frac{dp}{dz} \quad (1)$$

where K_o is the specific permeability, η fluid viscosity, dp/dz the pressure gradient, and f the true porosity (greater than the interparticle porosity f_o for a packed column, and $f = 1$ for an open column). The specific permeability for a packed column is given by

$$K_o = \frac{f_o d_p^2}{2\phi'} \quad (2)$$

where d_p is the particle diameter, and ϕ' is a dimensionless flow resistance parameter which has a value of about 300 as experimentally verified for well packed granular materials ($f_o \approx 0.4$). Hence, for laminar flow the velocity in a packed column is related to the particle diameter from (1) and (2) by

$$v = \frac{-\phi d_p^2}{2\phi' \eta} \frac{dp}{dz} \quad (3a)$$

where $\phi = f_o/f$ and varies between 1 for non-porous particles (e.g., glass beads) and 0.5 for porous particles (e.g., diatomaceous earth), but rarely $\phi < 0.5$; for an open capillary column the velocity is

$$v = \frac{-d_c^2}{32\eta} \frac{dp}{dz} \quad (3b)$$

where d_c is the diameter of the capillary. The carrier gas velocity varies throughout the column length L since the same mass of gas must pass through each cross-section in unit time. The velocity is the largest where the pressure is the least, namely, at the column outlet. The velocity v at any distance z in the packed column is given by

$$v = \frac{p_i v_i}{\sqrt{p_o^2 + \frac{2\phi' \eta p_i v_i}{\phi d_p^2} (L-z)}} \quad (4a)$$

where p_i and p_o are the inlet and the outlet pressure, respectively, v_i the inlet fluid velocity, and L is the column length; the velocity in the open capillary column is

$$v = \frac{p_i v_i}{\sqrt{p_o^2 + \frac{32\eta p_i v_i}{d_c^2} (L-z)}} \quad (4b)$$

Most conventional chromatographs operate within the range of laminar flow, but turbulence in chromatographic flow allows advantages in gas analysis. The degree of turbulence is given by the well known Reynold's number R

$$R = \frac{\rho v d_p}{\eta} \quad (5)$$

where ρ is the density of the fluid. Turbulence is achieved in packed columns for $1 < R < 100$ (for $d_p \approx 200 \mu m$) whereas for straight open tubes R must exceed 2100. The effect of turbulence modifies the pressure gradient in (1) by the additional term in v^2 given by

$$-\frac{dp}{dz} = av + bv^2 \quad (6)$$

where a and b are dimensional constants. From (6), turbulence causes an increase in flow resistance. The effect tends to equalize the velocity distribution in the channel cross-section as characterized by a flattened velocity profile. This decreases temporal spreading in a given zone (region of a given specie of the gas in the column) as it diffuses through the column and consequently, permits better resolution in detection. Figure 1 shows the zone sharpening for the turbulent flow as compared to the laminar flow.

Resolution in a gas chromatograph is a measure of the degree of separation of zones for two adjacent gas components. For example, upon injecting a 2-component gas impulse into the column inlet the gas components will separate into zones as it propagates down the column. The zones will be Gaussian in shape with σ defined as the half-width of the zone at half-maximum amplitude. The resolution is given by

$$R_s = \frac{\Delta z}{4\sigma} \quad (7)$$

where Δz is the distance between centers of gravity of adjacent zones of the two components of the gas as shown in Figure 2. The distance Δz increases directly as $\sqrt{HL}$, where H is defined as the theoretical plate height; therefore, when these parameters are substituted in (7), the resolution becomes

$$R_s = K\sqrt{\frac{L}{H}} \quad (8)$$

where K is a dimensionless quantity. The theoretical plate height is given by

$$H = A + \frac{B}{v} + Cd^2v \quad (9)$$

where $\bar{v}$ is the average velocity of the carrier gas, d takes the subscript d_p (the particle diameter) for a packed column and for an open capillary d takes the subscript d_c (the channel width), and A , B , and C are factors that relate to molecular diffusion and to adsorption-desorption kinetics. For a given chromatograph and gas specie the resolution in (8) is a maximum for a minimum H as obtained from (9) for an optimum velocity $\bar{v}$. With respect to channel size d_c or particle size d_p the resolution can also be maximized by minimizing d_c or d_p for either a capillary or packed column, respectively. The first two terms in (9) can be physically adjusted in order for the dominant control to be exerted by d in the third term. The resolution is determined from (8) and (9) approximately as

$$R_s = \frac{K' \sqrt{L}}{d} \quad (10)$$

In maximizing R_s , d cannot be decreased without limit, e.g., for a packed column the particle diameter limit is about 2 or 3 μm without getting into problems of colloidal suspensions, and for an open capillary a channel width of 1 or 2 μm can be achieved.

Design considerations for a miniature chromatograph allow scaling from a conventional chromatograph. A conventional packed column has an average particle size of a few hundred micron and is approximately 0.5 m in length. For the miniature gas chromatograph column, assuming similar ϕ and η , the pressure gradient has to increase by 100 to retain the same fluid velocity for a decrease in particle size by a factor of 10 as determined from (3a). For the same input pressure for both columns, the column length must be approximately 100 times shorter or about 0.5 cm in length. Therefore, the separation (or retention) time also becomes 100 times shorter, into the sub-second range for the miniature gas chromatograph. The shorter retention time requires a response time less than a few millisecond for both the gas sample injector and the detector. The resolution in zone separation is unchanged when the particle diameter and the column length is properly scaled. For the condition where the dominant control in plate height is determined by the particle diameter d_p , the resolution from (10) is $R_s = K' \sqrt{L}/d_p$ for the packed column. R_s remains a

constant if d_p is reduced by a factor of 10 and L is reduced by a factor of 100, thus verifying the assumption of unchanged resolution in the miniature chromatograph as compared to the conventional packed column.

For detection considerations, an open capillary system is competitive to a packed column for $d_c < d_p$. The system should consist of multiple capillaries having a common inlet and a common outlet with a total cross-sectional area approximately equal to that of the packed column. For the same resolution, the required open capillary length will probably be greater than that of the packed column.

3.0 MINIATURE COLUMN TECHNOLOGY

Microelectronics fabrication techniques are now available to micro-machine 1 to 2 μm channel width for open capillaries, and to backfill small width grooves for packed columns. The process that allows such high spatial resolution is based upon photolithography. The required geometry on a photomask in contact with the photoresist-coated Si surface is exposed with UV light. The photoresist polymerizes in the irradiated areas. When developed the irradiated photoresist adheres and the non-irradiated areas rinse off readily from the Si surface for a negative type photoresist. Hence, a geometric pattern can be engraved into the Si-surface by using a proper etchant. If the pattern is an array of straight lines which are oriented approximately parallel to a set of intersections between one set of $\{111\}$ planes and the (110) surface of the Si wafer, then deep, vertical-walled grooves can be formed with a selective etchant. An indication of typical dimensions that can be achieved are shown in Figure 3. Groove widths of 2 μm and 100 μm depth have been achieved with 10 μm center-to-center spacing. Obviously with these small dimensions, very long columns can be fabricated into the Si wafer. The short channels interconnecting the long grooves are relatively wide since they are not in the prescribed orientation. A thin quartz sheet can be electrostatically bonded to the Si surface, thus providing a means to cap-off the capillary column. The total length of the column can be appreciably long. For example, for a 2 x 2 cm square wafer, with a 10 μm center-to-center spacing, the total column length is 20m; however, such a narrow long column is not practical because of the excessive pressure drop in the column. A typical open-capillary column system may consist of

an array of 100 channels with a common input and a common output. Because of the increased resolution with decreasing channel width the column length can be reduced substantially as given by (10); a 10 cm column length for a 2 μ m channel should be adequate.

Packed columns can be fabricated also by using shorter lengths of about 0.5 cm and channel grooves of 200 μ m diameter without the orientation requirements for the deep narrow grooves in Si. The channel can be backfilled by chemical vapor deposition (CVD) techniques. For a 200 μ m channel, the average particle size of the backfilled material should be less than 20 μ m for uniform packing. For example, the reaction of oxygen with a silane-nitrogen mixture gives a porous SiO₂ layer at low temperature. After the grooves have been filled-up with the porous SiO₂, the structure (after removing the SiO₂ from the Si surface) can be capped-off with a CVD deposit of either dense polysilicon or SiO₂ layer as shown in Figure 4. An attractive feature of the miniature gas chromatograph is the ability to have multiple columns in one system, each sensitive to a class of gases. Each column can be backfilled by CVD methods with a different porous material that is the most sensitive to a particular gas or to a class of gases.

4.0 MINIATURE CHROMATOGRAPH SYSTEM

Conceptually, the miniature chromatograph has the flow diagram shown in Figure 5. The system has 3 valves; B is a fast-action valve, and the other two are slow-action valves. The inlet at the column is operated with a carrier gas at a few atmosphere pressure. For high sensitivity detection application the outlet at the column is operated at a vacuum of about 10⁻⁵ atm; otherwise, for low sensitivity application the outlet can be operated at ambient atmosphere.

4.1 Gas Injection System

The gas sample injector system is shown in Figure 6. Both valves A and B are diaphragm-type operated in a check-valve mode, i.e., normally closed to their respective ports. The carrier gas is contained in a pressurized pencil-sized canister having a needle-type valve that is connected to the input-port A. The inner diameter of port A is about 200 μ m. The design of the manifold allows unrestricted

flow of the carrier gas around the check valve B and thence into the chromatographic column. After the gas sample is introduced into the sample reservoir, port D is capped-off. The piston is then actuated to compress the gas. When the pressure in the reservoir exceeds the carrier gas pressure in the manifold, the check valve B opens and thereby admits the sample gas into the manifold. The desired open gate-time for valve B is less than a few milliseconds. The driving force on the piston head requires a very fast-actuating mechanism. Several mechanisms are being considered for the fast-actuated valve; these are 1) shutter-type mechanism as found in a camera, 2) piezo-electric impulse drive, and 3) a solenoid type drive. A purely mechanical type drive is preferred in order to minimize electrical power requirements for the chromatograph system.

4.2 Detector System

The detection system can be designed for either low or high sensitivity. The low sensitivity detector system may be useful for application in reaction gas analysis, for auto exhaust emission standards maintenance, and other applications not requiring more than a few percent sensitivity. Trace gas or contaminant gases require very sensitivity detection, in some cases, less than 1 ppm.

4.2.1 Low Sensitivity Detector

A miniature thermistor at the outlet operated at atmospheric pressure allows a simple but reliable means of detection. As the separated gas zones appear at the outlet, a slight temperature change occurs in the thermistor that corresponds to the gas specie. This change in temperature in the thermistor gives rise to an electrical signal whose amplitude is proportional to the amount of the specie.

4.2.2 High Sensitivity Detector

The detector consists of a high field ionizer. Ionization of the

outflowing gas from the column can be performed with an array of field-emitter points either in a mode similar to that used in a field-ion microscope, or by reversing the polarity of the field in an electron ionization mode. In either case a plasma is created. The charges can be separated to their respective collectors. The threshold detection level will be relatively high even in a vacuum environment (without a vacuum, the detection level would be much higher). Since the gas analysis in general will be for a molecular mass much higher than the carrier gas (e.g., He, Ar or N₂), an electrostatic analyzer is used to separate the heavy ions from the light ions. The analyzer is designed to be miniature, and its function only is to separate grossly the heavy ions from the dense concentration of light ions. In this manner, a low background level is achieved for the heavy ion collector and thereby an enhanced detection sensitivity. It should be pointed out that specie identification at the heavy ion collector is still made on the basis of temporal separation. The detector system is shown in Figure 7. A curvilinear plate electrostatic analyzer can be used. The light ions are more easily deflected than the heavy ions. An aperture (covered with a transmitting mesh) in one of the plates allows the heavy ions to impinge on an electron multiplier channel (EMC) (e.g., a Bendix Channeltron). Secondary electron emission at the input of the EMC allows ions to be detected with very high sensitivity (single electrons can be counted in a Bendix Channeltron). Specie identification is estimated to be less than 1 part per million.

A final comment should be made on samples that are so low in concentration density that the sample gas cannot be dynamically analyzed. In this case small selective filters can be used to integrate the contaminant molecules by adsorption, e.g., in an overnight period. The capsules containing the filter and a heater element can be connected to the input-port D of Figure 6. With the sample reservoir evacuated by an external pump and subsequently valved-off, the filter is heated to desorb the contaminant

molecules into the reservoir. Chromatographic analysis then follows as previously described.

The vacuum pump is the most power consuming component in the chromatograph. Two approaches requiring electrical energy are being investigated: 1) a miniature motor having a torque of 2.5 g-cm that requires 4W and has a dimension of 0.5 cm diameter and 2.5 cm length, 2) and a piezo-electric transducer in a resonating cavity that develops an axial oscillatory translation. After vacuum pump-down the power requirement for the piezo-electric transducer is appreciably less than that of the rotating motor; however, geometry and very high voltage requirements may not permit small packaging with the piezo-electric transducer. Investigations are being made also in the design of a vacuum pump using the jet power from the carrier gas canister either to rotate the shaft of the pump or to power a simple aspirator. The volume of the vacuum system for the detector system is estimated to be less than 8 cm³.

5.0 SUMMARY

Significant advances in the miniaturization of gas chromatographs can be made by using micro-electronics technology. Open-channel capillaries can be made by utilizing the very narrow (~2μm) deep (~100μm) grooves that can be preferentially etched into Si. Also, packed columns of a few hundred μm in diameter can be backfilled with porous compounds (about 20μm particle size) by chemical vapor deposition techniques. With the trade-off in the square root of channel length to channel width or particle size, considerable shortening of the column length can be made without any loss in resolution as compared to a conventional chromatograph. Detection sensitivity can be enhanced considerably by operating the ionizing detector in vacuum. For heavy gas detection, separation of heavy ions from a light ion carrier gas in a miniature electrostatic analyzer can enhance also the threshold detection level.

Table I presents the parameters for the miniature chromatograph system for both the open capillary type and the packed column type. An attractive feature of the packed column is to fabricate multiple columns each sensitive to a particular gas. A multiple manifold output-port system can connect via miniature valves to the desired column. One detector system can service all of the columns.

TABLE I

Parameters for the Miniature Chromatograph

$p_i = 2 \text{ atm}; v_i = 10 \text{ cm/sec.}$ $p_o = 10^{-5} \text{ atm (for high sensitive detection, 1 ppm)}$ $p_o = 1 \text{ atm (for low sensitive detection, 1 pph)}$	
packed column	open capillary
$L = 0.5 \text{ cm (length)}$ $d_o = 200 \text{ } \mu\text{m (channel diameter)}$ $d_p \leq 20 \text{ } \mu\text{m (particle diameter)}$	$L = 10 \text{ cm}$ $2 \text{ } \mu\text{m} \times 100 \text{ } \mu\text{m (channel cross-section)}$ 100 multiple channels

Additionally, for monitoring a single specie of gas in a one column chromatograph, considerable simplification in the output electronics is afforded since only one reference gate at a given time delay is required for recording the signal. For a thermistor type of detector the entire chromatograph is envisioned to be packaged eventually into a wristwatch-sized package.

The output electronics will consist of hybridized IC chips to amplify and process the output signal. By using A-D conversion any desired alpha-numeric format presentation is possible. A most convenient format being the time-delay to specie correlation for a specified chromatographic column and the specie concentration given by the amplitude of the output signal.

Useful references to chromatography are:

- 1) J. C. Giddings, Dynamics of Chromatography, Part I, Marcel Dekker, Inc., N.Y., 1965.
- 2) P. G. Jeffery, and P. J. Kipping, Gas Analysis by Gas Chromatography, The Macmillan Co., N.Y., 1964.
- 3) J. Krugers, Instrumentation in Gas Chromatography, Centrex Publishing Co., Eindhoven, The Netherlands, 1968.

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Fig. 1 - Pulse sharpening with turbulent flow.

Fig. 2 - Separation of zones for 2-component gas.

Fig. 3 - Preferentially-etched channels in Si.

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Fig. 4 — CVD porous SiO₂ backfilled into etched channels in Si with a CVD dense column cap.

Fig. 5 — Chromatograph System

Fig. 6 — Gas Sample injector

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