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A High Performance Hand-Held Gas Chromatograph

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A High Performance Hand-Held Gas Chromatograph

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Abstract

Gas chromatography is a prominent technique for separating complex gasses and then analyzing the relative quantities of the separate components. This analytical technique is popular with scientists in a wide range of applications, including environmental restoration for air and water pollution, and chemical and biological analysis. Today the analytical instrumentation community is to working towards moving the analysis away from the laboratory to the point of origin of the sample ('the field") to achieve real-time data collection and lower analysis costs.

The Microtechnology Center of Lawrence Livermore National Laboratory, has developed a hand-held, real-time detection gas chromatograph (GC) through Micro-Electro-Mechanical-System (MEMS) technology. The total weight of this GC is approximately 8 pounds, and it measures 8 inches by 5 inches by 3 inches. It consumes approximately 12 watts of electrical power and has a response time on the order of 2 minutes. The current detector is a glow discharge detector with a sensitivity of parts per billion. The average retention time is about 30 to 45 seconds. Under optimum conditions, the calculated effective plate number is 40,000.

The separation column in the portable GC is fabricated completely on silicon wafers. Silicon is a good thermal conductor and provides rapid heating and cooling of the column. The operational temperature can be as high as 350 degrees Celsius. The GC system is capable of rapid column temperature ramping and cooling operations. These are especially important for organic and biological analyses in the GC applications.

Key words
Microelectromechanical systems
MEMS components
Hand-held gas chromatograph.

Introduction

Gas chromatography has proven to be a reliable method for identifying unknown chemical mixtures. In a GC, an unknown chemical mixture is first injected and pushed by a carrier gas into its separation column. In the separation column, the chemical mixture is distributed between two phases, a mobile and stationary phase. The mobile phase is transported by a carrier gas in the separation column, and the stationary phase is adsorbed into and desorbed from a solid. Based upon the kinetics of the adsorption-desorption process in the gas-solid interface in the column, different chemicals achieve different moving speeds in the carrier gas. Within a precise column length, the chemical mixture can be separated into various components and recorded by the detector. For the conventional GC, detector sensitivities are at parts per million for thermal sensitivity detectors and parts per billion for various ion cell detectors. Chemical components are identified through their retention times—the traverse time for each of them as they pass through the separation column.

The separation efficiency of the GC column is related to the degree in which a solute band broadens (a function of the width of the peak, w) relative to the length of time the band requires to traverse the column (retention time t_R). The number of theoretical plates n is defined as ,

$$n = 16\,(t_R/w)^2 \tag{1}$$

Or, the number of effective theoretical plates is defined as,

$$N = 5.56\,[(tR - t_M)/w_{1/2}]2 \tag{2}$$

where t_M is the duration for non-adsorbed gases to traverse the separation column and $w_{1/2}$ the half line-width of a signal peak. The efficiency of a separation column is measured by the number of theoretical plates per unit length or the "height equivalent to a theoretical plate" h (HETP),

$$h = L/n \tag{3}$$

where, L is the total length of the separation column, or the "height equivalent to one effective theoretical plate" H (HEETP),

$$H = L/N \tag{4}$$

The hand-held GC has a wide appeal for numerous applications, such as on-site real-time toxic gas monitors, pollution detectors, reaction gas analysis, and law-enforcement usage. To ensure high detection sensitivity, a glow discharge detector (GDD) has been developed. In the GDD, operational voltage in all practical cases is a constant. Because of high conductivity in the plasma region, its operational voltage V(p) mainly equals the voltage-drop in the cathode dark region. Its operational current is locked by an external resistor. Therefore, it is also a constant. From Fowler and Nordheim's Equation of Field

Emission, the electric field E on the surface S of the cathode should also be a constant as is its charge density on the surface of the cathode. They are related and can be written as,

$$\varepsilon_o E = \sigma \tag{5}$$

where, σ is the surface charge density. This electric field E in the glow discharge is caused by the surrounding positive ions and the external applied electric field.

As gas mixture passes through the GC column, it separates into different sample plugs in the carrier gas. As these sample plugs pass sequentially through the glow discharge detector (GDD). some of their molecules are ionized. Depending upon their molecular ionization potential and the design of GDD, these ions from the trace elements exist at different distance and location on the surface of the cathode. In that duration, the surface electric field on cathode is modified. In a GDD, it can be written as,

$$I = I(0)*\{1(+/-)[E^{2}/E(0)]*\exp[-6.83*10^{(9)}*\varphi''^{(3/2)}*v(y)/(\delta E)]\} \tag{6}$$

where I(0) is the original current, E the electrical field on the surface of the cathode, E(0) the original electrical field before the sample plug, φ'' is the average work-function related to both ions, v(y) is the Nordheim elliptic function and the δE is an added field due to the sample's ions. The v(y) is normally close to a value of 1. With a proper designed GDD, all positive ions of the trace elements will be located behind the helium ions to causing the electrical field on the surface of the cathode to increase. From Eq. 6, only the positive sign will apply. The electrical current will increase and thus reduce its operational voltage or vice versa, however, as the operational voltage decreases, the cathode dark region decreases and the distance between the ions and the cathode decreases. Depending upon the structure of cathode, the electric field on the surface of cathode will further increase. Since under ambient conditions this distance between the ions and the surface of cathode is in the order of few tens or hundreds angstroms, is a relatively small than the area of surface, and, therefore, the relation of parallel plate electrodes can be used. One can show,

$$\rho = (1/V)*(\delta E)^{2} = (1/V)*[1/\ln(\text{signal voltage})]^{2} \tag{7},$$

where ρ is the sample concentration. Because the electric current is exponentially related to the surface electric field on the cathode, GDD is highly sensitive with a large dynamic range. The Center's experiments have shown that the GC can detect normal hydrocarbons in parts per billion and for electron-capture-chemicals, parts per trillion or more.

Experiments

With the GDD connected in series with a silicon separation column, carrier gas (helium) purges from the injector port through the silicon column and towards the GDD detector. Various concentrations of C_1 to C_5 hydrocarbon mixtures (from 2.8 parts per million to 0.68 parts per billion) were injected into the system and the sample column was separated into small plugs. These sample plugs were transported by the carrier gas towards the (GDD). The voltage change on the GDD was measured then plotted against the sample concentration. In Figs.1 and 2, the signal amplitude of C_5 is shown against a sample concentration. In Fig. 1, thesample concentration is from 2.8 parts per million and down to 0.68 parts per billion. In Fig. 2, an expanded version of the lower region of Fig. 1, shows sample concentration from 350 parts per billion and down to 0.68 parts per billion.

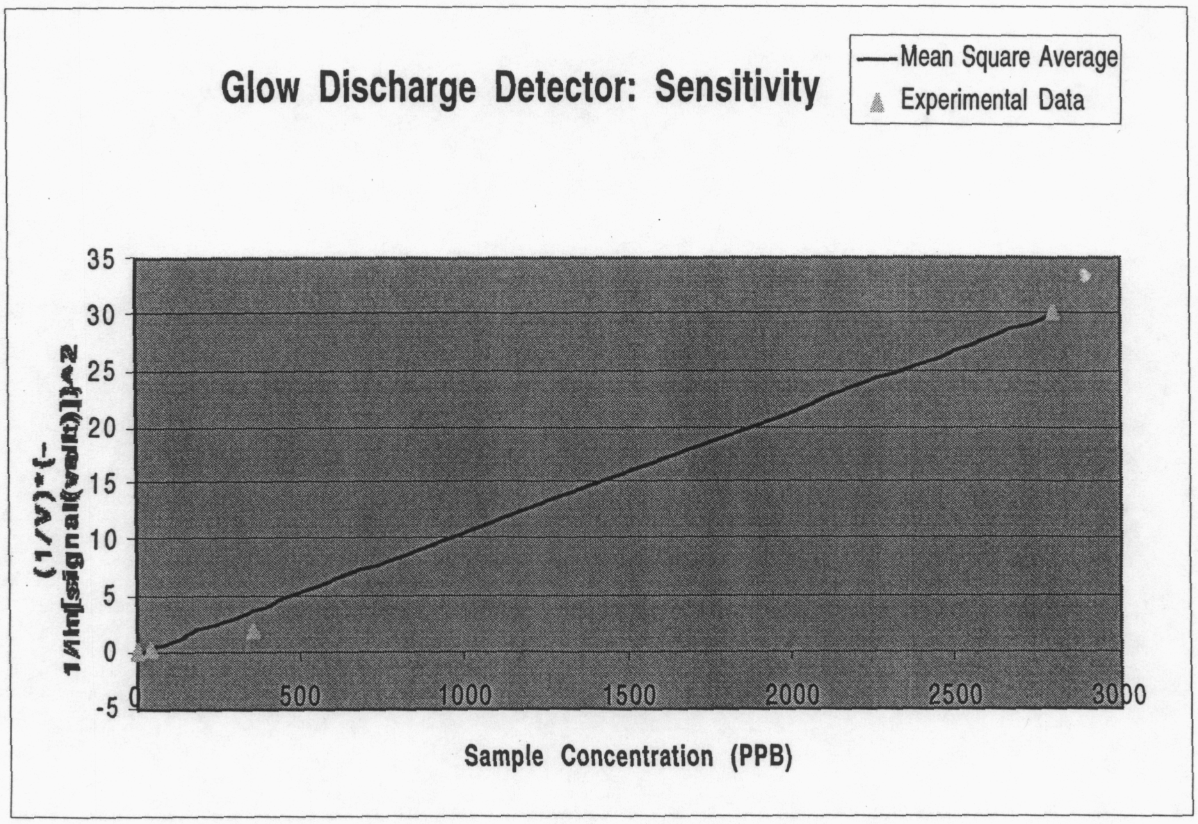

Figure 1

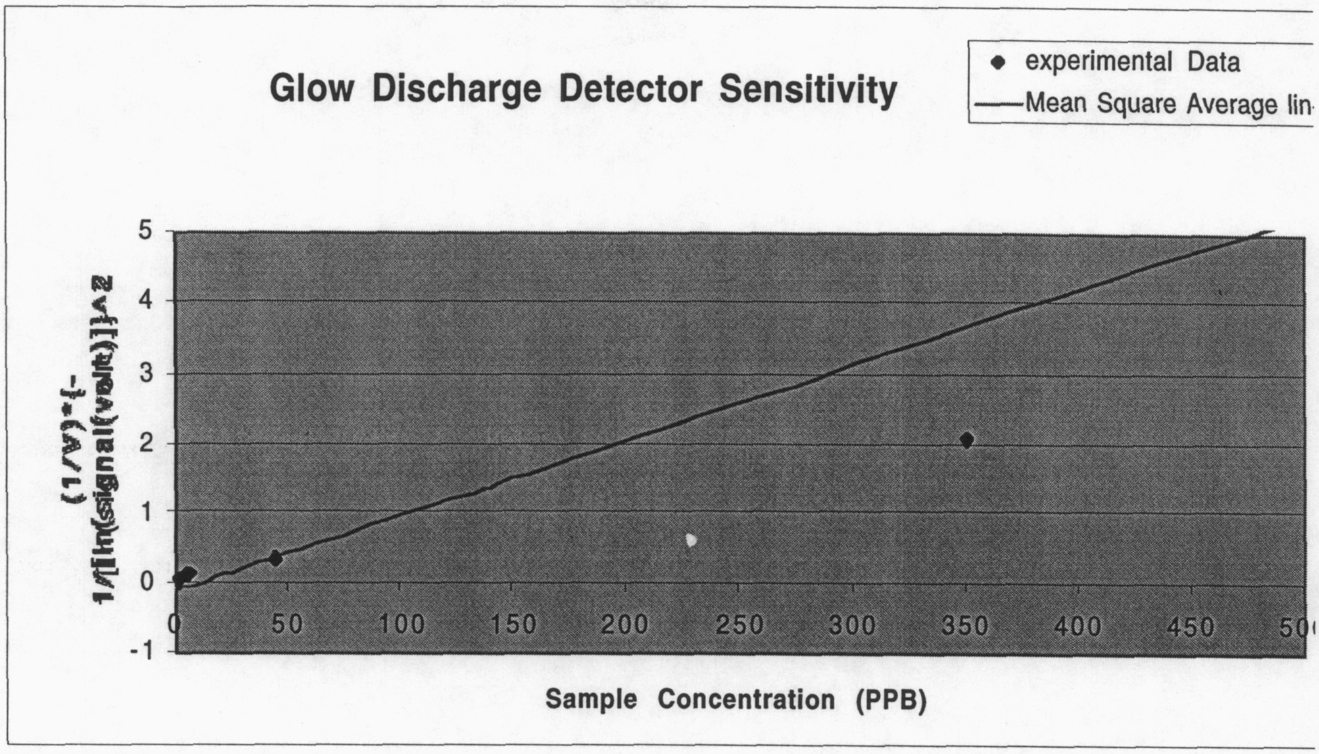

Figure 2

Discussion

Similar to a conventional GC, this high performance hand-held GC (HPHGC) consists of four major components: the sample injector, the silicon separation column, the silicon heater, and the GDD detector with related electronics. The present HPHGC's injector is a modified version of the conventional injector. Its separation column is fabricated on silicon wafers by means of MEMS technology. This separation column has a semi-circular cross section and spiral, six meter long with a diameter of 100 micrometers. The column heater was implanted on the back-side of the silicon wafer using a photolithography process.

From Fig.1, the data shows that to o.68 parts per billion, the signal detected through the GDD is positive in amplitude. The GDD does not show any instability in the detection range of 1000 parts per million to 1 parts per billion, a six orders of magnitude change of sample concentration. Therefore, this detector is well suited as a portable gas chromatograph application for high sensitive measurement.

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