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Gas Chromatography for the Undergraduate Student

ALEXANDER MACDONALD¹, JR. AND RONALD T. PFLAUM¹

Abstract. Gas chromatography has attained a position of prominence as a separation technique and as a tool for qualitative identification and quantitative determination. As such, it should rightly be discussed and applied in the undergraduate curriculum. A gas chromatograph suitable for teaching purposes has been designed and constructed in this laboratory. Experimentation applicable to the undergraduate laboratory is presented.

In the past ten years, gas chromatography has advanced to its present position of prominence as an important analytical technique. Wide acceptance and extensive literature attest to its versatility and utilization. Chemistry students entering industry or graduate school should be familiar, therefore, with the theory, instrumentation, and applications of gas chromatography. This paper describes a chromatograph and experimentation that can be used in the undergraduate laboratory to fulfill this need.

Gas chromatography is briefly described in many of the more recent texts on instrumental methods of analysis^{20, 40, 47, 53}. Several general reference works have excellent chapters on the subject^{6, 30}. Three relatively new books deal exclusively with gas chromatography. Keulemans' book²⁸ serves as the most general reference work presently available. *Gas Chromatography* by Bayer⁵ is concerned mainly with technique and application. Pecsok's *Principles and Practice of Gas Chromatography*³⁸ contains an extensive bibliography and is designed for a short course about the method. Reviews¹³ and published symposia^{37, 44} acquaint the reader with the recent literature.

Proper training in gas chromatography requires familiarization by the student in the use, operation, capabilities, and limitations of the apparatus. Versatile chromatographs for this purpose are offered by a number of manufacturers⁹, but high cost precludes their use as teaching tools. Several relatively inexpensive instruments⁵⁴ are likewise available, but these are limited in scope and can not be readily adapted to a wide experiment program.

INSTRUMENTATION

The gas chromatograph constructed in this laboratory is suitable as a teaching or research tool. The instrument was constructed from readily available components at a cost of less than

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\$200 exclusive of the recorder. Many of the components used are common laboratory items which can be disconnected from the instrument and reused in the laboratory. This chromatograph is rugged, versatile and was constructed easily and quickly. Other "home-made" chromatographs have been described in the literature^{2, 10, 14, 15, 18, 21, 23, 36, 45, 46}.

The unit with the exception of the battery and gas supply, is contained in a 17" x 22" x 38" cabinet mounted on a movable base. The unit could also be constructed as a table model. All controls, with the exception of the flow adjust, event marker and temperature control, are mounted on the front panel. The temperature control, together with the sample injection block, is located on the top of the instrument.

The chromatograph consists of certain basic components and can best be described in terms of a gas flow system, heating oven,

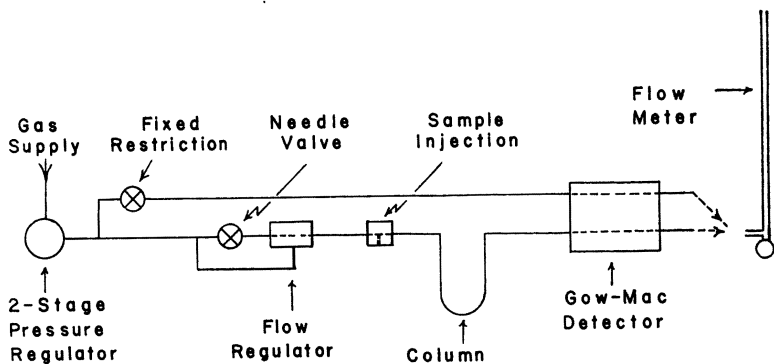


Figure 1. Flow System of Chromatograph

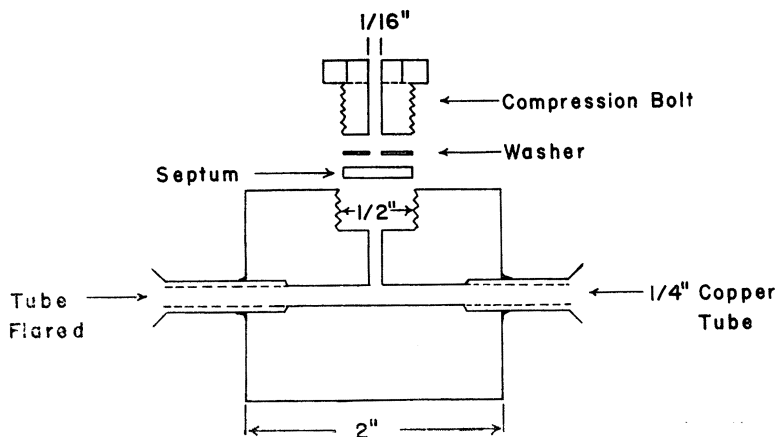


Figure 2. Sample Injection Block

operating controls and the detector. The gas flow system used is outlined in Figure 1. Copper tubing, $\frac{1}{4}$ ", with flared fittings is used throughout the system. A Moore flow regulator Model 63BU (Moore Products Co., H and Lycoming Streets, Philadelphia 24, Pa.) and an Ideal needle valve (Model 52-2-11, Ideal-Aerosmith, Inc., 3913 Evens Ave., Cheyenne, Wyoming) provide excellent flow regulation in the sample stream. A low flow (5-8 ml/min) is maintained through the reference stream by crimping a section of the copper tubing to provide a fixed flow resistance. The sample injection block (Figure 2) was made

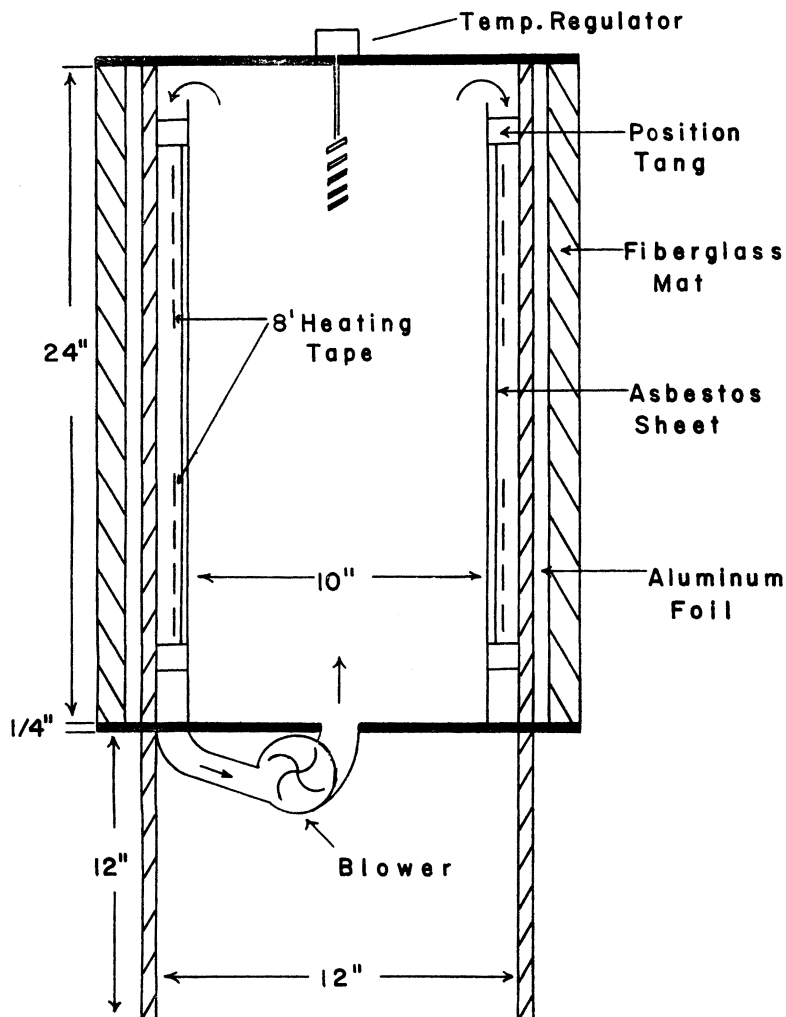


Figure 3. Heating Oven of Chromatograph

from a section of 1¼" brass hex rod. The block is heated by a 8" heating tape. The septum was made from ¼" Silastic 50 (Dow Corning Corp., Midland, Michigan). The detector is a Gow-Mac Model 9285 Pretzel type thermal conductivity cell (Gow-Mac Instrument Co., 100 Kings Rd., Madison, New Jersey). Flared brass fittings were silver soldered directly to both the inlet and outlet tubes of the detector. Chromatographic columns, 1½ to 24 ft., were prepared from ¼" copper tubing. Glass paper slugs of "Dexiglas" (C. H. Dexter and Sons, Inc., Windsor Locks Conn.) were used to retain the packing. A soap film flow meter⁵ was used to measure the gas flow.

The heating chamber was constructed from two sections of 12" diameter transite tube as shown in Figure 3. A two or three foot high oven could be selected by proper placement of the ¼" transite base plate. The transite tube was wrapped with aluminum foil and a one inch fiberglass mat. The inner pipe of the oven was made from a 22" section of 10" diameter sheet metal heating duct. The metal tube was positioned in the transite tube by three one inch metal tangs spot welded at the top and bottom of the metal tube. The metal tube was wrapped with asbestos paper and two 8 ft. by ½ inch heating tapes ("Brisket" Model B-8½ Briscoe Mfg. Co., Columbus, Ohio.) were then wrapped around the asbestos layer four inches from each end. Air circulation was achieved with a centrifugal blower (Burstein-Applebee Co., 1012-14 McGee Street, Kansas City 6, Mo.) mounted on the base plate with a duct to the space between the tubes. The regulator thermometer, injection block, and tubing connections are mounted on the ¼" transite cover plate. The detector and column are suspended in the oven from the cover plate.

The block schematic for the power wiring is shown in Figure 4. All components requiring 110 v. A.C. powe rhave separate con-

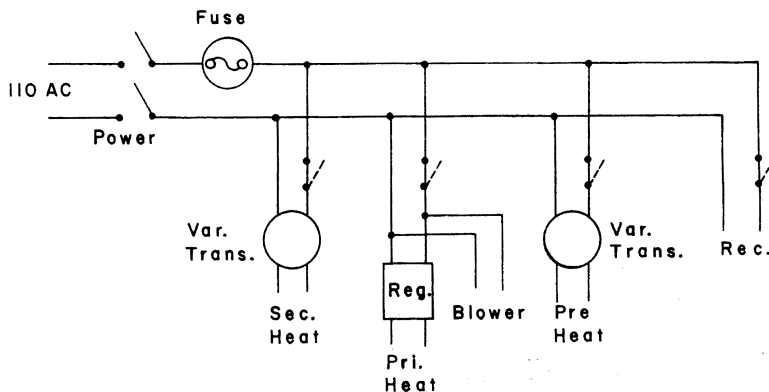


Figure 4. Control Wiring Diagram of Chromatograph

trol switches which are connected to a main fused power switch. The lower heating tape in the oven is designated as the secondary heater and is controlled by a variable transformer. The heating tape on the injection block is designated as the preheater and is also controlled by a variable transformer. The upper heating tape in the oven is designated as the primary heater and operates directly from the 110 VAC on a on-off basis dependent on the Aminco "Quickset" Bimetal Thermoregulator Model 4-239B (American Instrument Co., Inc., 8030-8050 Georgia Ave., Silver Spring, Md.).

The thermoregulator can be used directly or with any of the alternate wiring diagrams supplied with it. The blower is controlled by the primary heater switch, thereby always providing air circulation when the regulator is in use. The temperature range of the above is from ambient to 200°C with temperature regulation of the air bath being $\pm 0.4^\circ\text{C}$ over this range.

The detector circuit shown in Figure 5 was furnished by the Gow-Mac Corp. for use with their detector. The recorder is a 4-speed, 0-10 MV span Varian Model G-11A (Varian Associates, Inst. Div., 611 Hansen Way, Palo Alto, Calif.)

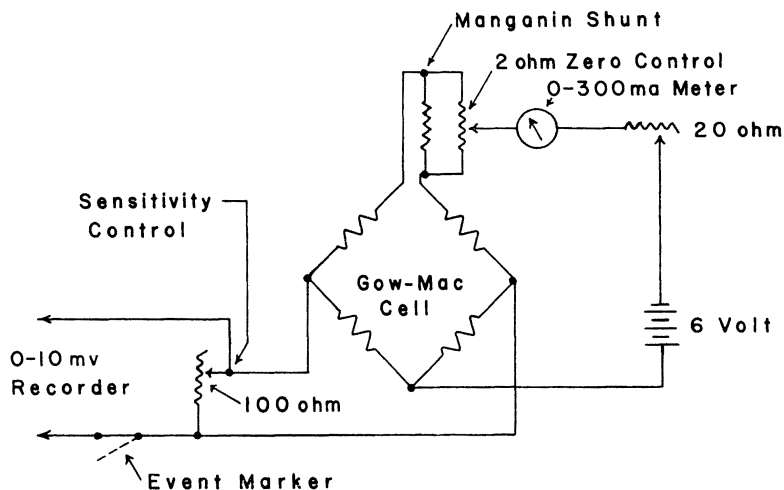


Figure 5. Detector Circuit of Chromatograph

DISCUSSION

The gas chromatograph described in the preceding section can best be constructed as a special project in an advanced level course. Since it is expected that construction will be followed by experimentation, and since every existing chromatograph requires definition of experimental parameters, we can assume that the following remarks concerning experimentation can be uni-

versal and independent of the nature of the instrument itself. The work cited can be carried out in courses involving the discussion and use of analytical instruments, in special projects courses, and in student research programs.

The extensive literature in gas chromatography contains innumerable possibilities of experiments suitable in the above situations. In the main, these can be classified into instrumental and chemical problems. In the former, operational procedures and the evaluation of operating parameters acquaint the student with the characteristics of the instrument and of the chromatographic technique. In the latter, analytical separations can be carried out to yield chemical data of both a qualitative and quantitative nature.

For efficient operation utilizing the full potentialities of the chromatograph, operating parameters of flow rate, heating rate, and temperature must be optimized. These instrumental requirements have been outlined¹⁸ and have been prescribed for precision gas chromatography⁴⁹. Equally important is a definition of the variables associated with the chromatographic column. The nature of the inert support (composition and particle size), the nature of the partitioning phase (composition and amount), sample size, and flow rate are all factors which must be evaluated. Both Bayer⁵ and Keulemans²⁸ explain and exemplify optimum conditions for these variables. The values of all parameters can be used as a permanent part of the operational procedure or can be reevaluated routinely as a recurrent instrumental exercise.

Turning away from the instrument, it is difficult to separate the chemistry of the sample from the chemistry of the reactive liquid phase in the column. The chemical nature of the partitioning phase is the determining factor in chromatographic separations. Information on the common liquid partitioning agents can be found in the literature.⁵ The choice of agent is naturally dependent upon the specific problem which is under consideration. In the following discussion, a number of chemical problems are discussed to illustrate the versatility of the gas chromatographic technique.

The aim of any analytical determination is to obtain qualitative and (or) quantitative data on the desired constituent(s) in a sample. Gas chromatography can and does yield both simultaneously. In addition, it can be used simply as a separation tool to yield pure samples of compounds. The major portion of the work carried out to date has been of a qualitative nature.

The use of gas chromatography in standard methods of qualitative identification has been very adequately discussed by

Keulemans²⁸. The study of chemical reactions by chromatographic identification of reaction products^{3, 43} has been advanced by several investigators. A method of qualitative organic functional group analysis⁵¹ using gas chromatography has been worked out. The application of multiple dissimilar columns to qualitative analysis³² has also been advanced.

Quantitative gas chromatography has been included in standard reference works^{5, 28} and outlined by numerous workers in the field^{18, 29}. Operational procedures and expected accuracies for a variety of samples have been prescribed^{49, 52}. The interpretation of chromatographic peak areas and the response of thermal conductivity detectors have been discussed by Brown⁸ and Rosie⁴² respectively.

There are many examples of simple concise analytical determinations that can be easily carried out in the undergraduate laboratory. Rapid carbon-hydrogen determinations involving standard combustion and gas chromatographic measurement of CO₂ and H₂O as such⁵⁰ or of CO₂ and acetylene (formed by the action of water upon calcium carbide) have been advanced^{19, 48}. The latter method is particularly well suited for student use since the apparatus requirements are simple. Using a 2-6 mg. sample, Duswalt and Brandt were able to achieve a precision of 0.5% for carbon and 0.1% for hydrogen with a total analysis time, including combustion, separation, and measurement, of 20 min.

Methods for the determination of carbon and nitrogen in organic compounds have been developed by Reitsem⁴¹. The method involves the combustion of the sample to CO₂, NO₂, and H₂O, the removal of the water with Mg(ClO₄)₂, and the gas chromatographic determination of the ratio of the two gases. The method can be modified for absolute nitrogen determination if CO₂ is used as the carrier gas.

Sulfur in organic compounds has been determined by Beuerman and Meloan⁷ using a combination of combustion and gas chromatography. Water formed in the combustion is removed using calcium sulfate and the CO₂ and SO₂ remaining are separated and measured by the chromatograph. The method has been used successfully with sulfoxides, sulfones, thiones, sulfides, disulfides, and thioethers with a relative error of less than 1%. The analysis requires about 20 min. and is not affected by the presence of fluorine, chlorine, nitrogen, or oxygen in the organic compound.

Gas chromatographic procedures have been advanced to yield a variety of information. Data on heats of adsorption^{11, 22}, relative surface area of adsorbents^{12, 26}, heats of vaporization³³, activity coefficients^{26, 31}, partition coefficients^{1, 39}, degradation re-

actions^{27, 34, 36}, and catalysis^{4, 16, 17, 24}, have been successfully obtained. All of these areas could be explored by the student. They would serve to emphasize the importance and the versatility of the gas chromatographic technique.

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The Direct Spectrophotometric Determination of Fluoride Ion

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Abstract. A direct method for the determination of fluoride ion in the parts per million range is described. The color reaction of fluoride ion and lanthanum chelate of 3-aminomethylalazarin-N,N-diacetic acid forms the basis for the spectrophotometric method. The intense blue fluoride complex in a mixed solvent system of 16% dimethylformamide-84% water is stable and independent of pH in the range of 4.6-5.6. Other halogens and common anions do not interfere in the measurements. Interfering ions are removed through ion exchange separations. Results on the determination of fluorine in selected samples are presented.

INTRODUCTION

The search for a rapid and direct method for the quantitative determination of fluoride ion has occupied the attention of chemists since the time of Berzelius (6). Volumetric (10, 11, 20, 21), colorimetric (9, 18), nephelometric (19), and gravimetric (13, 14, 16) methods have been developed in addition to a number of spectrophotometric methods (7, 8, 12, 15). These methods require complicated procedures or time consuming distillations and careful control of variables. The presence of diverse ions often causes interference; phosphate, sulfate, and chloride ions being especially troublesome.

While alizarin derivatives have long been used in indirect colorimetric methods (20), the possibility of developing a direct

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