



Portable Gas Chromatographs

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Instrument Performance Criteria

Portable Gas Chromatographs

Mary Lynn Woebkenberg, Column Editor

Reported by G.E. Burroughs and M.W. Tabor

Introduction

Portable gas chromatography (PGC) as utilized in the fields of environmental chemistry and industrial hygiene is an adaptation of one of the most frequently utilized techniques in organic chemistry analysis. To produce instruments which are “portable,” the manufacturers of the instruments described below have reduced both the size and weight of the analytical equipment, yet at the same time included options such as internal batteries and cylinders for carrier gas not necessary for laboratory instruments.

In a discussion on portable analytical instruments in general, Newman⁽¹⁾ wrote: “Like the personal computer, succeeding generations of analytical instruments have shrunk in size and weight even as they have become more sophisticated and versatile.” In addition to PGC, Newman’s paper on portable instruments discussed other analytical techniques including mass spectrometry, X-ray fluorescence, and infrared spectrometry, and he included as “portable” units up to a hundred pounds. Portable GCs discussed in the current article are well under half that weight, and have been developed from the base up as innovative designs rather than shrunken versions of existing instrumentation. For the purposes of this article, a PGC will be one which weighs less than approximately 50 pounds (20 kg), and is capable of operating independently of external power.

PGCs currently available on the commercial market are a compromise between an instrument easily used in the field and an instrument with full laboratory capabilities. Limitations of PGCs will be discussed below, but it should be

understood by the reader that it is not the intention of these instruments to replace the lab unit in all of its capabilities. For example, portable instruments must compromise between the need for power required to achieve high temperatures (greater than approximately 100° C) or temperature programming, and the need to minimize weight by limiting battery size. One concession universal to the instruments discussed in this review is that they all accept injection of a gaseous sample, while most lab instruments will readily accept a liquid sample injected into a heated injector for vaporization.

Certain concessions also have been made in instrument specificity and sensitivity. There seems to be a tendency, as will be noted in the citations below, to discuss these instruments in terms of “field screening methods” or other qualifiers. Although there certainly are those who would disagree, particularly among the manufacturers of the instruments which tout their PGCs capability to “identify” unknown compounds and quantify extremely low levels of analytes, it is the opinion of these authors that the better PGCs, in general, lack the capabilities of the better lab-grade instruments. They do, however, perform certain functions which their lab counterparts cannot.

Operating Principles

GC is a technique for the separation and quantification of chemical compounds where the compounds to be separated are distributed between solid or liquid stationary phases and a gaseous mobile phase. Selective retention of some types of compounds over others, based on factors including vapor pressure, polarity, and other physicochemical properties allows for the separation in a mobile carrier gas stream. Quantifica-

tion of the separated components is then achieved by a detector which uses one of a number of physical principles to produce a response to that component. GC is a comparative technique in which both the identification and quantification of analytes is based on the comparison of retention time in the column and detector response of those analytes, respectively, with samples of known identity and concentration. It is possible for two or more chemical compounds to have the same retention times, and therefore it is possible to incorrectly identify a substance and/or over-estimate its concentration. The use of multiple columns or detectors for verification (correlation chromatography) can minimize this problem, but is seldom done with PGC. The use of absolute methods of detection based on an intrinsic physicochemical property of the analyte (e.g., mass spectrometry) is beyond the scope of this presentation.

It is useful to visualize a GC as having three component parts:

1. an injector where the sample is introduced into the system, typically by syringe or by loop injection;
2. a chromatographic column, open tubular (capillary column) or packed, which contains the stationary phase which effects the separation of the various components of the sample; and
3. a detector which responds to the individual components as they exit separately from the column. Chromatographic columns for GC instruments are frequently categorized as polar, non-polar, or intermediate, depending on the properties of the compounds being separated. Detectors used in commercially available PGCs include

the photoionization detector (PID), the electron capture detector (ECD), the flame ionization detector (FID), and the thermal conductivity detector (TCD).

PIDs utilize an ultraviolet lamp which emits photons of sufficient energy (commonly 10.2 and 10.6 eV) to ionize many organic compounds. The resulting ions are collected and amplified to produce the signal. In an FID, the separated components of the sample are burned in a hydrogen flame and the ions resulting from this process are collected and amplified to produce the signal. The ECD (and functionally similar argon ionization detector, AID) uses a radioactive source (^{63}Ni or ^3H) which ionizes carrier gas, forming free electrons which create a high standing current at the collector. When a sample elutes into this detector, it captures some of the electrons, and the resulting decrease in standing current is measured as the output signal from the detector. The TCD does not ionize the analyte molecules, but, instead, depends on the differential ability of various compounds to conduct heat (thermal conductivity). As the carrier gas passes across a heated resistance wire incorporated into a Wheatstone bridge circuit, it cools it at a fixed rate. When analyte eluting from the column passes across that wire, it cools it at a different rate, changing its temperature and therefore its resistance. The resulting change in voltage is the detector output.

Selected general characteristics (compiled from chapter 7, McNair and Miller⁽⁴⁾) are presented in Table I.

A comprehensive introduction to chromatography is presented by Tabor.⁽²⁾ For a review of GC theory and techniques, as well as a description of various detectors, including over 6 ionization detectors, 6 optical detectors, and other miscellaneous detectors, with over 400 references, the reader is referred to Eiceman, Clement, and Hill.⁽³⁾ Another valuable reference on GC is the text by McNair and Miller.⁽⁴⁾ Reviews of recent research in gas chromatography, including a short section on PGC, are published in *Analytical Chemistry* in June of even numbered years. This alternates with reviews of applications, including recent research in industrial hygiene, air pollution, and environmental analysis, published in June of odd numbered years.

Applications

It is difficult to compile a list of tasks for which PGC is commonly used because routine applications seldom are published. However, a review of the literature does indicate that the technique is being used for a variety of applications. In the field of industrial hygiene, PGC analysis has been used not only for measuring time-weighted average and short-term exposure limits, but also for exhaled breath analysis,⁽⁵⁾ to measure the penetration of protective clothing material by various organic compounds,⁽⁶⁾ and to assure safe entry into confined spaces.⁽⁷⁾ NIOSH has published five analytical methods in its manual of analytical methods for the use of PGC in monitoring volatile compounds in exhaled breath,^(8,9) tracer gas for ventila-

tion studies,⁽¹⁰⁾ and organic compounds in the workplace.^(11,12)

The use of PGC to monitor soil and water contamination appears to be another area of interest. Headspace analysis of groundwater for petroleum hydrocarbons⁽¹³⁾ and of soils for VOCs⁽¹⁴⁾ and trichloroethylene⁽¹⁵⁾ have been reported. A purge and trap technique has been used for VOCs in both soil and water,⁽¹⁶⁾ and other techniques have been used for aromatic and chlorinated hydrocarbons in soil.⁽¹⁷⁾ There was even a report of relatively non-volatile PCBs in soil and sediment measured by PGC.⁽¹⁸⁾

Hazardous waste site investigations have also utilized the technique to look at low molecular weight organic compounds⁽¹⁹⁾ and VOCs,⁽²⁰⁾ and for the identification and measurement of "hazardous spills."⁽²¹⁾ Other published reports include the use of PGC to measure fumigants in food⁽²²⁾ and to analyze for organic compounds in ambient air.^(23,24)

Currently available PGCs allow samples to be introduced directly from the environment, or to be collected in inert plastic bags or evacuated containers for injection. Samples can come from ambient, workplace, or confined space air; from the space above or within liquids or solids; or from exhaled breath. Any of a variety of techniques can be selected for the collection and introduction of samples into PGCs.

Evaluation

Even though there are only a small number of PGCs on the market, no evaluation was found in the published literature testing all or even several of these in the laboratory or in the field. This is not surprising, given not only the cost of such an evaluation, but also the diverse applications of these instruments. What was found, however, were sporadic reports comparing one or two PGCs with other techniques.

Wang and Clifford⁽²⁵⁾ presented a study comparing aqueous headspace standards with SUMMA canister air standards where they used a Photovac 10A10 PGC and a HP 5890/5970 GC/MSD laboratory instrument to analyze

TABLE I
Selected general characteristics

Type	Selectivity	Minimum detectable quantity	Linear range
PID	Aromatics	10^{-12} g	10^6
TCD	All compounds	10^{-9} g	10^4
ECD	Halogens (and other electronegative compounds)	10^{-9} to 10^{-9} g	10^3 to 10^4
FID	Organic compounds only, no fixed gases	10^{-11} g	10^6

both. They looked at seven aromatic and chlorinated hydrocarbons. The Photovac and the HP produced values slightly lower than the calculated concentrations for these standards, but both instruments were usually within 10 percent of the calculated concentration and within 10 percent of one another.

A paper published in 1987 discussed one of the earliest applications of capillary columns in PGC.⁽²⁶⁾ A Photovac model 10A10 was retrofitted with a wide-bore capillary column and this system was shown to be capable of PPB sensitivity for several aromatic and halogenated hydrocarbons in the field. In the time since this work was done, wide-bore capillary columns have become standard in most commercial PGCs.

Berkley et al.⁽²⁴⁾ compared two identical PID GCs with each other and with passivated canister analyses for trace VOCs. They stated that the two techniques "do produce equivalent data," although the correlation between them was not quantified. They concluded: "Because the PCG can process data immediately, it is of great value for rapid screening of hazardous waste sites, chemical spills, and other sources of airborne organic vapors."

Limitations

One of the first questions frequently asked when the use of PGCs is considered is cost. An expenditure of approximately \$20,000 can be anticipated to establish PGC capabilities. This needs to be balanced not only against the cost of monitoring by other techniques, but also the need for increased or different operator training. Another consideration regarding the use of PGC is the transportation of both equipment and supplies. Compressed gases (for carrier gas or instrument calibration) cannot be taken aboard passenger aircraft either as checked or carry-on luggage, and the same is true for instruments with radioactive sources such as ECDs.

Specific detectors can also introduce limitations or advantages inherent to their operation. As stated previously, PIDs are somewhat selective and quite

sensitive for aromatic hydrocarbons, and depending on the energy of the photon source are more or less insensitive to many other compounds. This is of benefit when analyzing samples in an air matrix, because the oxygen and nitrogen of air produce no detector response. However, other compounds of potential interest, such as CO, CO₂, CH₄, and many of the quick take downs also produce no response on a PID. Early models of stand-alone PIDs (not used as a GC detector) have been shown to be affected by relative humidity.⁽²⁷⁾ This does not appear to be the case with newer detectors when used at a PGC detector where the unit is heated to slightly above ambient temperature.⁽⁷⁾

ECDs are somewhat selective and quite sensitive for electronegative elements and less sensitive to many other compounds. This produces a situation analogous to the PIDs discussed previously.

Manufacturers List

Baseline Industries, Inc.⁽²⁸⁾

760 W. Main St.

P.O. Box 649

Lyons, CO 80540

800-321-4665

Detector: PID

Data system: menu-driven operation, graphical display, data downloadable to PC

Foxboro⁽²⁹⁾

33 Commercial Street

Bristol Park (B51-2C)

Foxboro, MA 02035

888-369-2676

Fax: 508-549-6703

Model: Century TVA-1000

PID and FID

Data system: menu-driven operation, on-board data logging, bar graph readout

Weight: 12 lb (5.6 kg)

Hewlett Packard⁽³⁰⁾

Little Falls Analytical Division

2850 Centerville Rd.

Wilmington, DE 19808-1610

800-227-9770

P series (formerly MTI Analytical Instruments, Model M200)

PC controlled

Available with 1 or 2 columns and detectors

"Solid state detector" (TCD)

Loop injection

Microsensor Systems, Inc.⁽³¹⁾

62 Corporate Ct.

Bowling Green, KY 42103

410-939-1089

Model MSI-301

Surface acoustic wave (SAW)

On-board computer

Perkin-Elmer Photovac⁽³²⁾

761 Main Ave.

Norwalk, CT 06859

800-762-4000

Models: 10S series, Voyager

syringe or sample loop injection

wide-bore capillary column

PID (ECD also in Voyager)

Data system: on-board microprocessor

Weight: 15 lb (Voyager)

Sentex Sensing Technologies, Inc.⁽³³⁾

553 Broad Ave.

Ridgefield, NJ 07657

201-945-6064

Model: Scentograph

AID or ECD

capillary or packed column

Isothermal or programmable oven

Data system: instrument control and data collection by PC

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