I. PORTABLE GAS CHROMATOGRAPHY

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1. INTRODUCTION

The term "portable gas chromatograph (GC)" as used here refers to any gas chromatograph not requiring external electrical connections. The portable GC may range in size and portability from a self-contained unit the size of a small suitcase easily carried by one person to a much larger unit requiring auxiliary gas supply and requiring more than one person to transport.

2. PRINCIPLES OF OPERATION

A portable GC consists of, at a minimum, an injection system, a separator (column), and a detector.

a. Injection

There are two basic injection systems: (1) gas-tight syringe through a septum [1] and (2) flushing and filling a sampling loop [2]. The loop is usually filled by means of an on-board pump. Injection is usually accomplished by means of a valve system, either manual or automatic.

The loop system is inherently more accurate, but the volume injected is fixed. However, sample loops are available in a range of volumes. The gas-tight syringe is not as accurate, but injection volumes between 10 L and 1 mL may be selected as appropriate for concentrations encountered in the field (the lower the concentration, the larger the injection volume). Both injection systems may require purging to reduce memory effects.

b. Separation

The sample is carried through the column by a carrier gas. Many systems have refillable gas

cylinders which must be charged before going to the field. Others may need exterior carrier gas cylinders and regulators. It is important to check the carrier gas requirements in the manual of instructions which goes with the particular portable gas chromatograph. It is also important to consider the appropriate shipping regulations concerning compressed gases.

Columns may be of two types, i.e., packed or capillary. The packed column can accept a larger injection volume, but the capillary column has better separating power. Therefore, the choice of a packed or capillary system depends on the complexity of the atmosphere to be sampled and the desired detection limit. It should also be noted that columns for portable GCs may require special geometries, material of construction and hardware specific to the instrument. The users manual should be consulted for information in this area.

The interaction between the injected sample containing one or more compounds in the vapor phase and a liquid phase present, e.g., on the walls of a capillary column or coated on a diatomaceous earth (solid support) in a packed column results in a separation. The stronger the interaction between the component in the vapor phase and the liquid phase, the more strongly the flow of the component will be retarded by the column, i.e., the longer the retention time, t_r [3].

The use of a heated column system greatly increases the flexibility of the analysis. As in any isothermal situation, there will still be a usable window of retention time. However, the retention time of any peak is a function of the temperature. As a rule of thumb, the retention time doubles for every decrease in column temperature of 30 C [4]. It is thus possible in many cases to select a temperature at which the peak of interest will have a usable retention time on a particular column.

c. Detectors

After the sample leaves the column, it goes directly to the detector. Detectors vary according to their selectivity, sensitivity, and linearity. The four most commonly used in portable GCs are as follows:

(1) Flame ionization detector (FID) [5] - large linear range; moderate sensitivity; good general detector for organics; low response to CS_2, CO, CO_2, CCl_4; non-selective; requires auxiliary gases (air and H_2).

(2) Photoionization detector (PID) [6] - large linear range; high sensitivity; good general detector for organics and some inorganic gases; generally lower response to some small molecules, i.e., CH_3CN, CH_2Cl_2, CCl_4, CH_3OH and low-M.W. hydrocarbons; selectivity can be introduced in some systems by using different energy lamps, if available.

(3) Electron capture detector (ECD) [5] - small linear range; high sensitivity; very selective - in general, responds to molecules containing halogen (fluorine, chlorine, bromine, iodine) atoms, cyano groups or nitro groups; minimal response to hydrocarbons, alcohols, ketones, etc.

(4) Thermal conductivity detector (TCD) [5] - good linear range; low sensitivity; general non-selective detector for volatile compounds including all organics, as well as inorganics such as ammonia, CO, SF_6, NO, NO_2, and SO_2.

The choice of detector, and, therefore, in most cases, the instrument, will depend on the chemical to be monitored, the nature of any other contaminants, and the sensitivity required.

d. Limitations

Most portable GCs have no provision for heating the column, detector, or injection port. This limits analyses to the more volatile compounds, and results in variation of retention times with ambient temperature. Also, late-eluting peaks will be poorly formed and will not be very useful for quantitation. This imposes a severe restriction on the number of usable column packings for any given contaminant. It also affects the ability of the system to work well in complex atmospheres, since all quantifiable peaks must have short retention times, and those with long retention times will appear as poorly-defined peaks which may interfere with quantitation of the well-shaped peaks of later injections. Consequently, if contaminants other than the one of interest are known or suspected to be present in the workplace atmosphere, it is essential that these compounds be considered when the selection of a column is made in the laboratory prior to field work.

There is a similar limit to the usable retention time region for a capillary column operated isothermally. Its advantage is that within this usable region it does more efficient separations. Some portable GCs have provision for backflushing the column, which is useful in removing strongly adsorbed compounds which are trapped on the front of the column.

An important point to remember is that an observed retention time does not constitute unequivocal identification of a contaminant; an independent, specific identification must be made to confirm the identity of any peak. However, the knowledge that the compound in question is in use or is likely to be present plus the presence of a peak with the expected retention time is strong evidence for the identity of the contaminant. Thus, some knowledge of the chemicals and the processes in use in the atmosphere to be examined is essential. Retention time on a second column of different retention characteristics is a valuable aid to identification.

Such important parameters as the detector drift with time, retention time variation with temperature, usable battery life, etc., should be determined in the laboratory prior to use in the field.

3. SAMPLING CONSIDERATIONS

a. Safety

The main safety consideration is the use of an FID in areas where a potential explosion hazard may exist. Do not use a detector of this kind in any area where a flame would not be permitted unless the instrument has been rated intrinsically safe. If an electron capture detector is used, the radioactive effluent must be safety vented.

b. Type of sample

In contrast to laboratory-type GCs, portable GCs do not have heated injection ports. Therefore, the sample must be a gas or vapor at room temperature. In general, whether the sample is introduced by means of a loop or a gas-tight syringe, most measurements give essentially instantaneous concentrations. Integrated samples may be taken, if desired, by using gas bags, evacuated gas bottles and the like; in that case, the sample concentration is averaged over the filling time of the sample container. It is important to use only those sample containers in which the analyte is stable.

c. Column Selection

Once the decision to use a portable GC has been made, in most cases, the critical question becomes the selection of the column. The following are some hints to aid in the selection of the column best suited to the analysis to be performed [3]:

(1) Retention time is proportional to column length.

(2) Retention time is proportional to the percent loading of the stationary phase.

(3) Column resolution is proportional to both loading and column length.

(4) Non-polar vapors (e.g., hydrocarbons, halogenated hydrocarbons) are separated most efficiently by non-polar stationary phases; polar vapors (e.g., alcohols, ketones, esters) by polar phases. Information on the polarity and selectivity of stationary phases is available in the form of McReynolds constants which are tabulated in the catalogs of various vendors of GC supplies. A useful discussion of the use of McReynolds constants for column selection appears in the catalog of Applied Science, Inc., 2051 Waukegan Road, Deerfield, IL 60015.

(5) Special columns have been developed for various types of separations. In the catalogs of most suppliers of GC columns there is a section on applications and many of the suppliers will be happy to discuss problems and suggest solutions.

4. DATA ACQUISITION AND TREATMENT

a. Types

Data acquisition may be done automatically or manually depending on the particular design of the portable GC. If the instrument does not have provision for automatic data collection,

then, in most cases, the output signal from the GC will have to go to some external data collection and storage device, usually a recorder. In such a display, the area under the peak of interest is proportional to the amount injected. However, peak height, to a reasonable approximation, can be considered proportional to the amount injected. This approximation is only true for measurements performed under identical conditions, i.e., identical column, identical temperature, etc. Thus if there are substantial changes in ambient temperature such as would be encountered, for example, in going from an indoor to an outdoor location, and the GC is operating at ambient temperature (unheated), then the peak height at each location must be related to a standard run under the same conditions.

b. Calibration

As mentioned before, column selection should be done in the laboratory before going into the field. Calibration should be done in the field. There are two reasons for this. First, the potential differences in ambient temperatures between lab and field could lead to errors as mentioned previously. Second, there is almost always drift in the response of detectors with time. Therefore, calibration should always be done as close to the time of actual use as possible. If experience shows that detector drift is significant over the period of time that samples will be taken, then it will be necessary to make frequent injections of standards during the course of the day. Even in the event that drift does not seem to be a problem, occasional injections of standards throughout the period of use is recommended to make certain that the instrument is operating as expected.

Calibration standards may be of two types: commercially available certified gas mixtures or gas bags prepared from a known gas or liquid aliquot of the desired compound plus a carefully metered volume of diluent, usually air or nitrogen. It is strongly advised that the preparation of standards be done in the laboratory as a practice exercise before attempting it in the field, and that the ability to produce accurate bag standards is verified in the laboratory by comparison with a standard concentration.

If the injection system operates by means of a loop, the calibration curve should be of the form of concentration vs. peak height (obtained from the recorder trace). If a gas-tight syringe is used, then the calibration curve is more conveniently of the form of amount (concentration, w/v, times volume injected) or volume (ppm times injection volume) vs. peak height. The range of standards should encompass the expected ambient concentration at the field site. If this is not known, then preliminary samples should be taken to determine the range of expected concentrations. Duplicate injections of each standard should be made and the average value used for the calibration graph. From the data on the precision of the calibration graph, information about the precision of the measurements and the limits of detection can be obtained using standard statistical methods.

c. Procedure

Once the calibration graph has been generated, the next step is to gather field data. This is done simply by injecting samples of the ambient air periodically into the portable GC and obtaining concentration values by comparison with the calibration graph. The frequency of sample taking is governed by the time necessary for the peak of interest to appear (retention time) plus the time necessary for any other contaminants to elute from the column. As it is seldom possible to know the exact composition of the atmosphere to be sampled beforehand,

the time between samples will usually have to be determined in the field.

d. Indications

Portable GCs find their most common use as a tool for the gathering of concentration data during industrial hygiene surveys. They may also be used for real time monitoring of leaks, spills, etc., in order to make a judgment as to whether or not a dangerous concentration may have been reached. Some instruments with microprocessor-controlled acquisition and storage of data may be used to assess trends over extended periods. An important consideration, however, is that portable GCs should not, in general, be used for compliance measurements, nor are they meant as substitutes for the usual analytical methods used for determination of exposure such as those in this Manual. There are basically two reasons for this. First, there is no provision for unequivocally identifying a peak obtained, such as could be done in the laboratory using a GC/mass spectrometer system, and second because the separation step in the portable GC is not, as explained previously, as efficient as that obtainable with a laboratory analytical instrument. It is equally important to point out that the field measurement is inherently much simpler and does not have the problems with incomplete adsorption and desorption, sample storage instability, migration, and breakthrough which some of the compliance methods have. Thus while the field measurement is less exact than would be the case with a laboratory measurement, the overall field sampling and measurement process may be, in fact, more exact.

5. REFERENCES

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