THE USE OF A PORTABLE PID GAS CHROMATOGRAPH FOR RAPID SCREENING OF SAMPLES FOR PURGEABLE ORGANIC COMPOUNDS IN THE FIELD AND IN THE LAB

BY

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ABSTRACT

A headspace technique is used to screen water, soil, and sediment samples on a portable gas chromatograph equipped with a photoionization detector and a 4-foot SE-30 column. The technique is useful for screening samples prior to their analysis by GC/MS to prevent excessive levels of organics from harming the GC/MS. Quantitative analyses can also be done directly on the GC by preparing headspace standards. Detection limits range down to ppb levels.

The same approach may be applied to real-time and time-weighted ambient air samples.

I. BACKGROUND

The Region I Laboratory, in fulfillment of its task to protect the environment, analyzes, routinely, a wide variety of samples including drinking waters, industrial wastes, soils, sludges, sediments, and ambient air.

Among many tests done routinely, the lab runs these samples for volatile (purgeable) organics. The EPA prescribed method for volatiles in water is our Method 624 (1), which requires analysis using a gas chromatograph/mass spectrometer (GC/MS).

The actual run time on the mass spectrometer for each analysis is about 30 minutes, plus time for data reduction, preparation and analysis of standards, plus quality control. If the first run for a sample is too dilute or too concentrated, a second run is required. Worse yet, ppm levels of organics will contaminate the GC/MS, requiring hours or days of time to free the instrument of contamination.

In order to avoid this down-time and to reduce the number of runs required, we have developed a screening technique which allows us to select a safe and proper dilution for the GC/MS analysis of each sample. Under certain conditions the screening can be expanded into a quantitation method.

(1) Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, EPA-600/4-82-057, July, 1982, (EMSL, USEPA, Cincinnati, OH 45268). This is an updated version of the method that first appeared in the Federal Register on December 3, 1979.

II. METHODS

A. Apparatus

The equipment required is listed in Table I.[2] The Photovac model 10A10 is shown in Figure 1. It measures approximately 16" long x 6" high x 9" deep. It weighs roughly 20 lbs.

This equipment is portable. The battery and the air-bottle will allow a full day's work in the field with the GC. They can be set up quite easily in a mobile van or even on a tail-gate of a station wagon, weather permitting. The column is designed to operate at ambient temperatures. Therefore, the GC and the samples need to be at the same, relatively stable, temperature in a location free of organic vapors. The surrounding temperature (room temperature) needs to stay relatively constant throughout the period of analyses so that elution time of compounds from the the column is reproducible.

B. Water

1. Sampling and Preservation

Water samples should be taken in duplicate following procedures in method 624[1]. If the samples are not to be screened and

(2) The mention of specific products or trade names does not constitute endorsement or recommendation for use.

analysed within 2-3 days, they should be preserved with 20 ul of 2.% $HgCl_2$.[3] Whether preserved or not, the samples should be refrigerated at 4°C. Field blanks should be taken also.

2. Sample preparation

At least one vial for each sample must be retained for the final analysis. Once a vial has been left at room temperature for any long period of time or has been opened, it is no longer usable for quantitative analysis. Those vials to be used for screening should be allowed to come to room temperature shortly before the screening is to begin.

In order to create the necessary headspace, first insert a disposable syringe tip through the septum to allow make-up air to enter the vial. Then invert the sample and remove 10 ml through the septum with a syringe. Remove the syringe and the syringe tip and rinse them thoroughly before proceeding to the next sample. (For the safety of the analyst, the withdrawal of the 10 ml is best done in a hood.)

Shake the sample vigorously for 60 seconds. The sample is now ready for analysis. (Keep the vial inverted at all times except when withdrawing headspace aliquots.)

(3) If chlorine is present, sodium thiosulfate is used as the preservative. See Method 624.

Recent information which has come to our attention leads to some modification of the protocol suggested for volatiles in soil and sediment.

1. Use 30 cc of water with mercuric chloride preservative for tared voa vial.
2. Very carefully and quickly transfer a small aliquot of soil (1 gm) from a core sample to the prepared VOA vial.
3. If analysis is not to be performed in the field using the headspace technique, return the filled sample vials to the laboratory inverted. This will help preserve volatiles from being lost thru the septum.
4. The rational for this procedure is that large soil samples will require several volumes of water to leach out high level organics. This is based on work of John Wilson et al at the Ada Labs.

3. Standards

Prepare, in a volumetric flask, a working level standard at the desired concentration range following the procedures in Method 624.(1) (We frequently use 40 ppb.) Carefully inject 1 ml of liquid mercury into a 160 ml serum vial. Immediately add 120 ml of the freshly-made working standard into the serum vial and crimp on the top. Invert the bottle and shake vigorously for 60 seconds. Keep the bottle inverted. The mercury will form an air-tight seal over the septum.

4. Screening

Set the air flowrate at 20-60cc/min. (If some flow of air through the GC is permitted 24 hrs/day, no instrument warm-up time is required.) Select an appropriate syringe. Place the standard vial upright, insert the tip of the syringe into the headspace and pump the plunger slowly several times. Fill the syringe slowly to the desired volume; then remove the syringe and quickly inject the aliquot onto the GC column. (At no time should any water be injected.) After the last peak has eluted, screen the samples in the same manner. If nothing is known about the samples, start with small aliquots (10-50 ul) of headspace and a low sensitivity scale on the GC (50 or 100 K). After the initial runs, headspace volume can be increased to 1 ml. Scale expansion can be altered as needed before or during each run.

C. Soils and Sediments

1. Sampling and Preservation

Samples for quantitative analysis are collected as follows:

1. All samples must be iced or refrigerated at 4°C from the time of collection until analysis.
2. Grab samples should be collected in glass containers of at least 40 ml volume.(4) The container should be filled as completely as possible and hermetically sealed.

   Note: The sampler should remember that the entire contents of the container will be treated as the sample. Any supernatent liquid will not be decanted before analysis.
3. All samples should be taken in duplicate or triplicate.
4. Field blanks are to be taken also. See Method 624, step 3.2.(2)

For headspace screening additional samples are taken as follows:

1. Add 20 ml of organics-free water and 20 ul of 2.5 mercuric chloride to a clean 40 ml "VOA" vial. Cap the vial with a septum style top and weigh vial to nearest 0.1 gram.

See above notes

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(4) Forty ml "VOA" vials are preferred unless the nature of the sample (e.g. it contains rocks or leaves) makes it difficult to get representative sample into a vial.

2. Record this as the tare weight.
3. At the sampling location, add approximately 10 ml of soil or sediment to the vial, leaving 10 ml headspace. Cap the vial, refrigerate it at 4°C, and return it to lab.
4. Weigh the vial and record this weight.

2. Sample Preparation

If vials for screening purposes were prepared as described above, these vials need only to be warmed to room temperature and shaken vigorously for one minute. If no headspace vials were prepared, weigh 1-10 grams of sample into a clean 40 ml septum vial. (Record the weight.) Quickly add sufficient organics-free water to create a total volume of 30 ml. Seal the vial and shake for 60 seconds.

3. Standards

The standards will be prepared in water as in part II.B.3 above.

4. Screening

Proceed as in II.B.4 above

III. DISCUSSION - WATER & SOIL-SEDIMENT

The headspace screening has reduced expensive GC/MS time and greatly reduced lost analysis time. We no longer risk accidentally overloading organics into the GC/MS. We can usually estimate the levels of organics

closely enough to allow the GC/MS operator to select the proper dilution.

If we have a series of samples with similar patterns of eluting compounds, we can select representative samples for GC/MS analysis rather than run all the samples on the GC/MS. When screening shows no organics to be present, we can often safely assume that no priority pollutants are present at the ppb level. There may be exceptions to this.

We usually prepare a screening standard containing several of the compounds we expect to find in the samples. A typical standard might contain 40 ppb each of o-xylene, toluene, tetrachloroethylene, trichloroethylene, and 1,1,1-trichloroethane.

Two potential disadvantages are: the insensitivity of the photoionization detector to linear chloro-alkanes and the problem of co-eluting peaks that occure in complex samples. The detection limits we have found for a number of volatile organics are listed in Table II. A typical chromatogram is shown in Figure 2.

The screening technique can be extended to quantitation if all the peaks in the samples can be identified.

If quantitation is to be done:

-the working standard should be freshly made.

-all injections for the samples and standards should be made with the same syringe.

-the injections should be at least 20% of the volume of the syringe (in order to get a more reproducible volume).

The intent here is not to imply that this headspace technique gives the same accuracy and information as is possible using GC/MS Method 624. However, for certain types of requests, the accuracy and precision of Method 624 is not required. For these purposes, analysis time can be saved by GC screening and quantitation.

IV. SCREENING AIR SAMPLES

Screening of Absorbed Air Samples

A. General Discussion:

The regional lab has also developed a preliminary method for the analysis of air samples for volatile organics. While it is not the purpose of this paper to get into a detailed discussion of this method, this work is mentioned because of its similarity to the headspace technique.[5] A partial list of the apparatus needed is shown in Table III.

In general, a sample is collected on previously cleaned Tenax[6] or coconut charcoal traps. Typical volumes for collected samples are 10 liters for Tenax and 30 liters for charcoal collected over 4-8 hours. The trap is then desorbed into a reservoir. Aliquots can then be withdrawn for screening on the PID or for analysis on a GC/MS equipped with a purge and trap device.

(5) For further information, contact Dr. Thomas H. Spittler or Ms. Moira Lataille at the Region I laboratory.

(6) Tenax: Trade name for a polymer available from Supelco, Inc. (Bellafonte, PA).

B. Standards

Concentrated standards in methanol are prepared as in Method 624[1] and small volumes of these are injected into 160 ml septum vials that are equipped with the mercury seal described earlier. These standards are injected at relatively high concentrations and small volumes in order to form standards in a vapor state. They are made daily.

C. Screening

Aliquots of the standard and the desorbed samples are injected into the portable GC. For this work, it is desirable to perform any quantitative GC/MS analyses concurrently with the screening.

V. ACKNOWLEDGMENT

The methods described in this article were developed by Dr. Thomas H. Spittler, Chief of the Technical Support Branch at the Region I Laboratory, and by the following staff of the Chemistry Section, in addition to the authors:
Dr. William J. Andrade, Dr. Kathleen M. Polgar, and Mr. Richard Giacanew.

TABLE I

Apparatus for GC Screening of Waters and Soils

1. Photovac Model 10A10 equipped with PID and a 4 foot SE-30 column
2. Air, "zero grade"
3. Recorder, variable speed, 100 mV full scale, battery operated
4. Syringes, assorted sizes 10 ul to 1 ml
5. Septum vials, 40 ml, with cap & septum, precleaned with soap and water
6. Serum bottles, 160 ml, with crimp-on tops and crimping tool (Wheaton Glass)
7. Balance, top-loading, to 0.01 gm
8. Analytical balance, to 0.1 mg
9. Liquid mercury
10. Pesticide grade methanol
11. Standards for purgeable organics of interest

TABLE II

Retention Times and Detection Limits for Some Priority Pollutant Volatile Organics

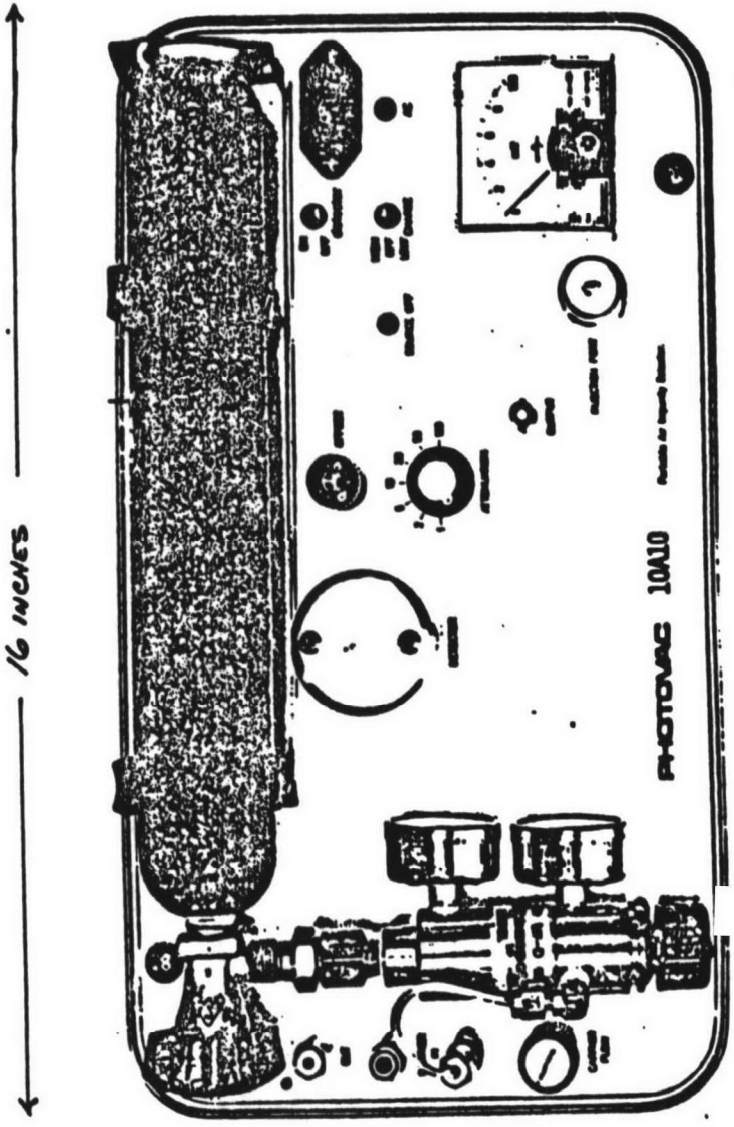
	Relative Retention Time (to Benzene)	ppb Detection Limit
Trans-1,2-dichloroethylene	0.45	<0.5
Benzene	1.00	<0.5
Trichloroethylene	1.40	<0.5
Toluene	2.55	<0.5
Tetrachloroethylene	3.80	<0.5
Ethyl Benzene	6.00	1.0
Methylene Chloride	0.35	3
1,2-Dichloroethane	0.85	40
1,1-Dichloroethane	0.35	3
1,1,1-Trichloroethane	0.85	10
Chloroform	0.65	5
Bromodichloromethane	1.40	20
Dibromchloromethane	2.90	20

Operating Conditions: .4-foot SE-30 column
.30 ml/min flow rate
.Assume 4 min peak
= minimum detectable

TABLE III

Apparatus for Screening Air Samples (Partial List - In Addition to Items in Table I)

1. Century Programmed Thermal Desorbed (Foxboro Co., So. Norwalk, CT).
2. Gas tight syringes.
3. Tekmar LSC-2 concentrator unit outfitted with a 5 ml Needle Sparge Kit (Tekmar Co., Cincinatti, OH).
4. Stainless steel traps containing coconut charcoal or Tenax[6] adsorbents supplied by the Foxboro Co.



View of top of Photovac's 10A10, showing [illegible] referenced in text.

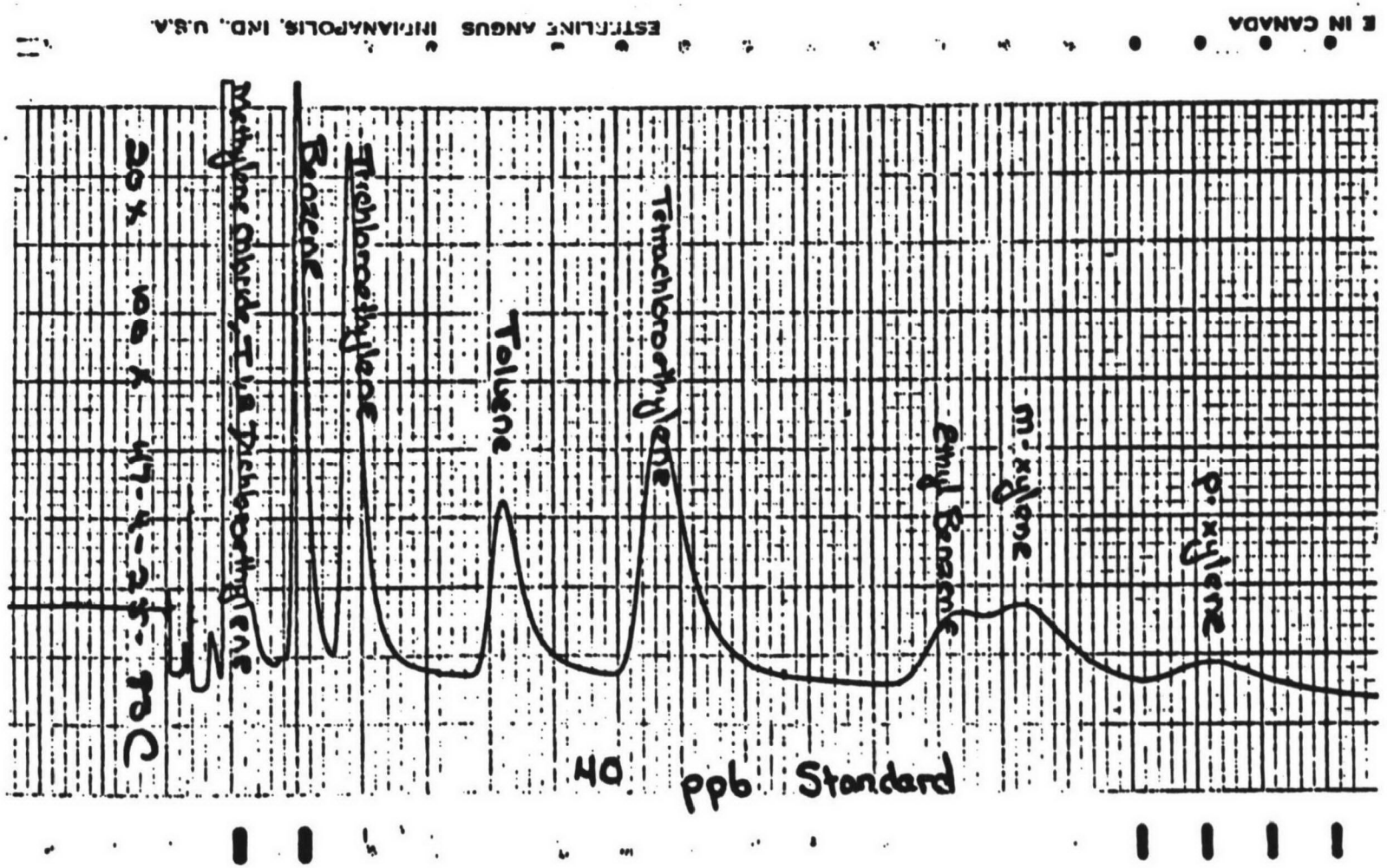


FIGURE 2.

A TYPICAL CHROMATOGRAM