

**Essential Capabilities of a Portable Gas Chromatograph \***

Richard E. Berkley  
US Environmental Protection Agency  
Research Triangle Park, NC 27711

**ABSTRACT**

Volatile organic compounds in ambient air are usually estimated by trapping them from air or collecting whole air samples and returning them to a laboratory for analysis by gas chromatography using selective detection. Data do not appear for several days, during which sample integrity could become compromised. Immediate data can be obtained, and sampling errors minimized, by analyzing with a field-deployable instrument at the time samples are collected. Portable gas chromatographs are available, but they don't fully meet the need for quick, high-quality data under field conditions. Shortcomings include insensitive detectors, non-selective detectors, poor resolution, retention time drift, maladroit data processing schemes, excessive energy consumption, and vulnerability to weather. Improved waterproofing, temperature regulation, and energy efficiency are particularly crucial to true field-deployability. Such improvements are probably feasible. Mass spectrometric detection, high-speed chromatography, polycapillary chromatography, and peak modulation may lead to useful enhancements in future.

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**INTRODUCTION**

Analysis of volatile organic compounds in air is usually performed on samples which have been collected in the field and transported to a laboratory. Samples are collected by trapping analytes on sorbents or by collecting whole air samples in canisters. Analytes are separated from the sample matrix by thermal desorption from sorbent media or by cryogenic preconcentration from the whole air samples. Then gas chromatographic analysis is performed using a selective detector. Mass spectrometric detectors are especially effective because they can detect most compounds selectively. Other specific detectors, such as electron capture or photoionization, may be used to achieve greater sensitivity [1]. Analyzing samples in a laboratory makes it possible to apply sophisticated techniques which yield data of good accuracy and precision. The data define the condition of samples at the time they were analyzed, but not necessarily at the time they were collected. Disadvantages are that sample integrity could become compromised during collection or storage, and data are not available for days to weeks after sample collection. Analyzing samples with a field-deployable instrument as soon as they are collected could finesse those problems. "Field-deployable instruments" are essentially

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self-contained units which can readily be lifted by one or two people. They are convenient to deploy at remote sites, require minimal logistical support, and can be shipped routinely by common carrier. By contrast, instruments permanently mounted in vehicles, mobile laboratories, and instruments which must be operated in on-site laboratories are not field-deployable instruments.

Commercially-available portable gas chromatographs (PGC) are the field-deployable instruments most often used to analyze volatile organic compounds in air [2]. The number of samples which one PGC can analyze at a field site far exceeds the number which can be sent to a laboratory for analysis because PGCs work faster and because they discard samples as they analyze them, keeping only the data. Prompt access to data and increased volume of data can help to characterize hazardous waste sites, chemical spills, and other unknown and potentially-hazardous sources of volatile organic compounds in air. They can also optimize the selection of samples to be collected for later laboratory analysis.

#### PORTABLE GAS CHROMATOGRAPH PERFORMANCE PROBLEMS

PGCs are not used as often or as effectively as they could be because they don't perform as well as laboratory instruments and because the advantages they offer are not well understood. PGCs do have inherent disadvantages. Most are not equipped for programmed-temperature chromatography because of constraints on size, weight, and power consumption. Since isothermal chromatograms cannot separate as many compounds, fewer compounds can be analyzed per run. Resolution may also be inferior to that of laboratory instruments. Some commercially-available PGCs suffer from inadequate design or shoddy components. Operators become discouraged, and loss of confidence in the instrument does not militate for greater proficiency. As a result, PGCs have been taken less seriously than they should be. When operated properly, they can produce data of good quality which can be meaningfully compared to data from laboratory analysis of concurrent, colocated samples [2,3].

Changes in instrument design and operating procedures are needed to bring the performance of commercially-available PGCs up to full potential. The performance of laboratory chromatographs may never be equalled, but there is no reason to accept less than achievable performance. Two changes which are not immediately needed are better capillary columns and smaller instruments. Presently-available capillary columns are adequate, and presently-available PGCs are smaller and lighter than they need to be. Most of them can be lifted with one hand, but connections to utilities, sample inlets, and data devices tie them down during operation. "Hand portable" or "pocket" instruments have limited use. They can locate "hot spots" at uncharacterized sites, if they are "hot" enough. That done, what is needed is to find out quickly which toxic compounds are present and how much of each. Hand-held instruments cannot do that, and laboratory analysis takes too long. An analytical instrument performing on-the-spot analyses would be ideal, even one larger, bulkier, and more costly than present-day commercially-available PGCs.

## Design Problems

When a PGC is unable to perform at full potential, it is usually because it was designed by people who don't use it, and compromises were made in choosing components to reduce size and cost.

Chromatographic Resolution. It is not necessary to use low quality flow system components, though it may seem expedient to do so. PGCs usually have lower resolution than laboratory instruments because they use shorter columns to reduce analysis time, but too often the other parts of the flow system are more rudimentary than the column. Resolution is degraded by solenoid valves if they are too large for the column or if they stick or leak, and active surfaces cause peak tailing. A selective detector can partially compensate for poor chromatography, but the number of compounds that can be analyzed is reduced, and so is accuracy.

Detectors. Some PGC detectors are insensitive or non-selective, for example, thermal conductivity and flame ionization. Using such "universal detectors" does not make it possible to analyze more compounds. They are relatively insensitive and may not notice trace amounts. Since no chromatograph can separate all the contaminants in ambient air, each peak generally contains two or three compounds, so identifications based on retention times using nonselective detectors are unreliable. If a detector cannot distinguish between coeluting compounds, then the "information" it provides is misleading, and its only real capability will be running calibration standards. A PGC detector needs to be both sensitive and selective. Photoionization and electron capture detectors meet these criteria and can readily be operated in the field. Simultaneous use of more than one kind of selective detector would increase the number of compounds which could be analyzed in each run. Mass spectrometers are more difficult to operate in the field, but the advantages they offer might make the extra trouble worthwhile.

Carrier Flow Control. Poor flow control causes variable retention times and unstable baselines. Many PGC manufacturers use needle valves to regulate carrier gas flow. Ordinary needle valves are rarely considered adequate for laboratory chromatographs, even though they usually operate in quiet, clean environments. Why expect a needle valve to cope with the jolts, vibrations, and contamination which are encountered in field operation?

Weatherproofing. Fluctuations in column temperature destabilize baselines and retention times. Worse yet, relative retention times change with temperature, compounding the chaos. Constant temperature is critical not only to column performance, but also to proper function of electronic components, especially signal-processing. Oven insulation in PGCs is sometimes perfunctory, and usually electronic components are not insulated at all, even though they must operate in environments where ambient temperature range is broad and access to line power is limited. At the first chill breeze, retention times go up, the baseline goes down, and response factors decrease. The ovens of laboratory chromatographs are usually well insulated, but they still use plenty of line power to control temperature. Temperature stability of their electronic components is left to the heating/cooling system of the laboratory building. If electronic components get too cold or too hot, performance suffers. Why build less temperature

control into a field-deployable instrument when it actually needs more? And why build a field-deployable instrument that will be ruined if it is left out in the rain?

Power Requirements. An instrument which must be plugged into a power outlet is useless without the power outlet. Instrument designers who believe that field operators cannot lift more than twenty pounds will not likely think of using a full-size 12 volt battery, but the weight is not significant unless there is a long walk to reach the site. Sites which are accessible to vehicles but have no line power are more common than hike-in sites which do have line power. Twelve volt batteries are generally more reliable than the line power at remote sites, and they are easier to obtain. Gel-cell batteries can be shipped by air. Marine batteries can be completely discharged many times without damage. They provide 80 to 100 ampere-hours, ample power for most instruments. If more power is needed, more batteries can be connected. It is probably easier to suppress electrical noise in an instrument which operates on 12 volt DC power. If a battery is connected to a 12 volt DC instrument while it is operating on line power, the instrument can charge the battery. Then in event of a power failure, the battery can supply power to the instrument. Portable generators offer an alternative, but they have their own disadvantages, including the possibility of contaminating the site with exhaust.

Microprocessor Control. Many PGCs are controlled by internal microprocessors. Too often they turn out to be too small to accommodate the multitude of schemes for exploiting them which come to mind after they have been selected. It would be better to design an instrument to be driven by an external laptop computer or even to build a computer into the instrument. A full-size computer memory would be capable of accommodating the kind of sophisticated peak recognition and measurement algorithms which are used in laboratory instruments. That would decrease the need for hand correction of misidentified peaks and "bad integrations". At least one manufacturer has already done this.

Data Processing. Some PGCs have built-in data-processing schemes which inhibit or even prevent the operator from choosing a preferred format for data tabulation. Access to data may be delayed, and data quality may even be impaired. At a minimum, the operator should be able to receive data on disk in a form which can be processed by standard data-reduction software. Hand-copying data is unacceptable because it risks contamination by human fingerprints.

Summary of Performance Problems. Most design problems result from compromises which are intended to enhance portability or reduce cost. There is no good reason for some of them to occur at all. Eliminating others will require substantial redesign. A few are inherent in portability and must be endured. Manufacturers can best work to mitigate functional problems by paying careful attention to how their products are used and periodically redesigning them to fit their real-world applications. Going off in a corner to invent cute-but-trivial new features may not improve sales. The most pressing problems don't call for great technological forward leaps; they should be tractable with current technology.

## POTENTIALLY USEFUL INNOVATIONS

There are several enhancements to gas chromatographic technique which might be applicable to field deployable instruments; however, none of them are specifically limited to portable instruments, nor are they potential remedies for poor design or inferior components.

### Mass Spectrometric Detectors

Mass spectrometers have long been used as gas chromatograph detectors. They are highly selective for most compounds and can often identify unknown compounds unequivocally, even when they coelute. There is at least one commercially-available field-deployable mass spectrometer which has a gas chromatograph attached to it. It can be lifted by two men and shipped as excess baggage on an airplane. It requires line power. If this instrument is sensitive enough, it could do on-the-spot quantitative analysis. If not, it might still validate data produced by other PGCs by positively identifying compounds.

### High-Speed Chromatography.

Levine has developed a field-deployable high-speed gas chromatograph which completes a chromatogram in less than one minute [4,5]. A specially-designed monel cryofocusing loop is heated by capacitive discharge to inject samples onto a capillary column, typically 0.25 mm inside diameter and 10 m long. Injection bandwidth is 10 msec, and carrier flow velocity is 60 to 175 cm/sec. A specially-adapted detector must be used to distinguish between peaks and electrical noise and to ensure that the outlines of peaks are well-defined. Detector response must be extremely fast, so conventional noise filtration cannot be used. This instrument has been successfully operated with flame ionization, electron capture, and photoionization detectors. Resolution is not compromised, and separations are enhanced by the narrow bandwidth of the injections. Sensitivity is also increased because narrow peaks are taller. As a result, it is possible to detect analytes at low part per billion concentrations in whole air samples of 0.25 - 5 ml. Disadvantages include use of line power and liquid nitrogen. Also, trace contaminants in the carrier gas tend to build up in the capillary trap, because it is cooled continuously between capacitive discharges. This instrument will be field tested during 1993.

### Polycapillary Gas Chromatography

Grachev and coworkers at the Limnological Institute in Irkutsk, Russian Federation have designed a fast gas chromatograph that uses a multitude of parallel glass capillaries which are close-packed inside a hexagonal sheath which is about 6 cm in diameter [6]. A schematic of its cross-section is shown in Fig. 1. Typical column length is 20 cm, and retention times for many compounds of low volatility, pesticides for example, are less than five minutes. Resolution is poor, but might be improved by changes in the injection system. This technology, referred to as polycapillary gas chromatography, may eventually be useful for analysis of high-molecular-weight compounds, especially pesticides.

### Peak Modulation.

If a microbore capillary column were used, column length could be reduced in proportion to bore diameter. Some scale reduction could also apply to analysis time. It is difficult to make an accurate injection onto a microbore column without flooding it. Phillips has found a practical way to do this using a peak modulator to chop samples of ordinary size into miniature aliquots as they emerge from a

capillary column of ordinary diameter [7-9]. The peak modulator consists of a short length at the downstream end of the capillary column which is coated with electrically-conducting paint. Electrical leads are attached to each end of the conductive section. When a pulse-sequence electric current is applied, the modulator is rapidly heated by each pulse and quickly cools to ambient temperature between pulses due to its low heat capacity. Each pulse expels from the modulator whatever analyte material has entered it since the last pulse. It departs the modulator in a narrow band and immediately enters either a microbore column or a detector. Setting up a peak modulator can be tedious, but that is not much of a problem if the same procedure is repeated indefinitely, as is typical of PGC applications.

One-Dimensional Microbore Capillary Chromatography. To inject a sample onto a microbore analytical column, the modulator is placed at the end of a short length of ordinary capillary column and connected directly to the head of the microbore column [7,8]. Flow is not split, so flow velocity is faster in the microbore column. Injection is made onto the short capillary, through which the sample travels at normal (relatively slow) velocity. As the injection band enters the modulator it is chopped into a sequence of miniature aliquots which pass through the microbore column at much higher velocity and are seen by the detector as a sequence of fast chromatograms. These are added together to produce a single chromatogram. This process is shown schematically in Fig. 2. In effect, the microbore column has analyzed a large sample in a few minutes without becoming overloaded. It produces a high-resolution chromatogram which would have taken much longer using a larger column.

Two Dimensional Microbore Capillary Chromatography. A peak modulator placed at the downstream end of a full-length large-bore capillary column will chop effluent into aliquots. Further separation is done on a microbore column immediately downstream which uses a different stationary phase. The resulting two-dimensional chromatogram can achieve separations which are impossible using a single column [9]. The process is shown schematically in Fig. 3, and a two-dimensional chromatogram is shown in Fig. 4.

Enhancement of Late-Eluting Peaks. A modulator can be placed at the end of an analytical column, just before the detector, as shown in Fig. 5. The peak of any compound which has affinity for the stationary phase in the modulator will be chopped into a series of tall, narrow peaks, the tops of which trace the outline of a peak which has the same width but is much taller than the original. This effect, shown in Fig. 6, increases as peaks become shorter and broader toward the end of a chromatogram, and it tends to rescue them from merging with the baseline, which is particularly a problem on isothermal chromatograms. The kind of stationary phase in the modulator will determine which classes of compounds are enhanced and which are not.

## CONCLUSIONS

Portable gas chromatograph performance has made great progress in the last 20 years. At present they can produce reliable on-site data rapidly, given adequate shelter, power, and operator skill. They are no longer novelties, but they are temperamental under adverse conditions, and some design modifications seem appropriate:

o PGCs are already easier to transport than necessary. Some portability could be sacrificed to solve other problems. An instrument which one person can stuff into the back seat or the trunk of a car would be portable enough, if it performed well in the field.

o Randomized retention times, peregrinating baselines, and wilting response factors are intolerable. Gas chromatographs operate best with column and electronic components at constant temperature. Field-deployable instruments need to be self-sufficient as to temperature stability. PGC columns generally operate isothermally, so why not enclose the entire system in an insulated and thermostatted box? Thermal leakage from electronic components and the (separately-insulated and thermostatted) column enclosure could provide auxiliary heat.

o Field deployable instruments should be rain-proof.

o Field-deployable gas chromatographs should be able to operate on battery power for at least eight hours, but preferably twenty-four hours.

o A major incentive to use a field-deployable instrument is to get quick and easy access to data. Any design feature which hinders data access is undesirable, no matter how attractive.

o The ideal PGC would perform as well in the field as it does in the laboratory.

o Once the performance of a PGC has been optimized, consideration should be given to integrating into it features such as mass spectrometric detection, high-speed chromatography, polycapillary columns, and peak modulation.

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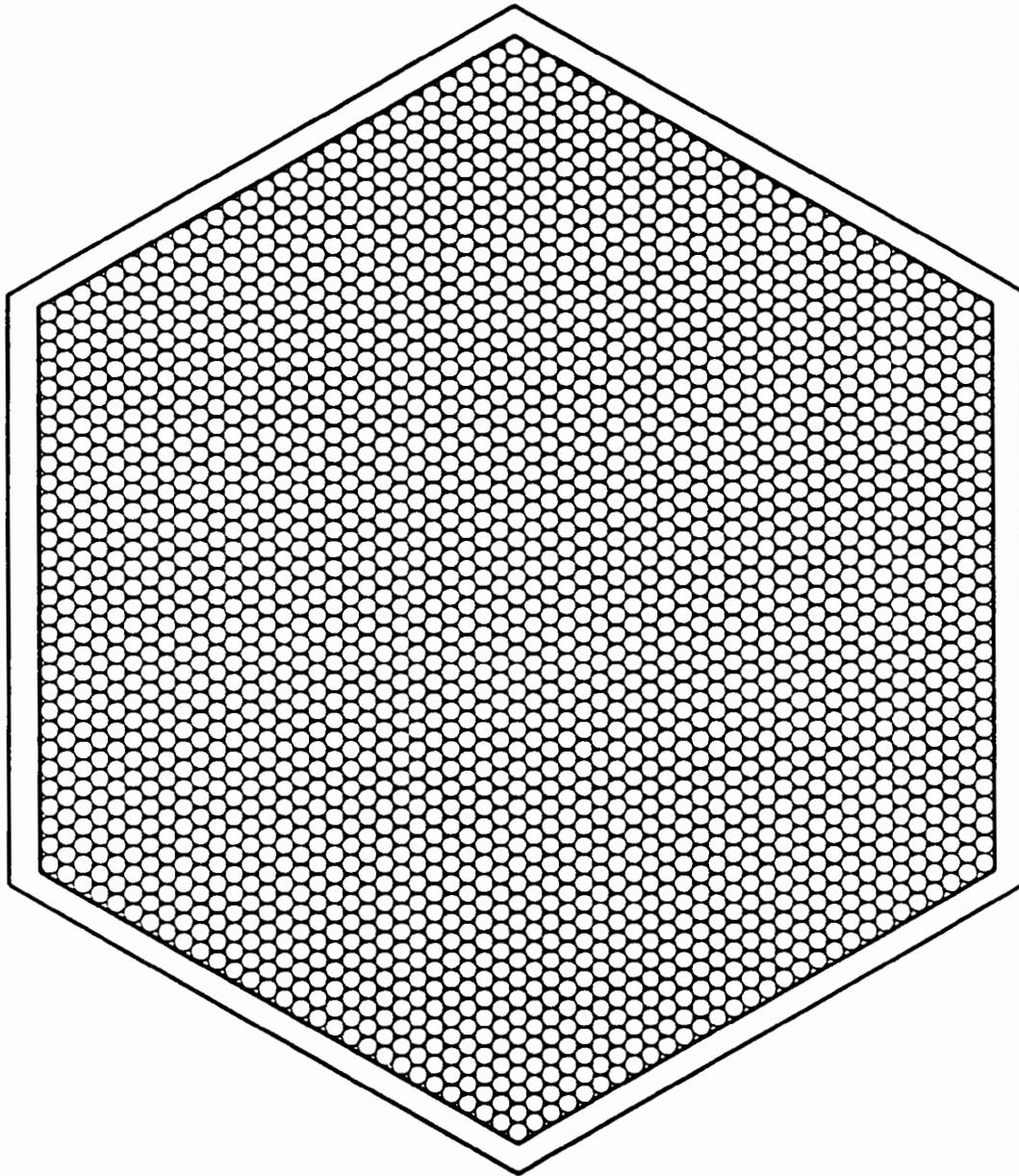


Figure 1. Cross-section of a polycapillary column. Length 20 cm, width approximately 6 mm. Not drawn to exact scale. The number of capillaries is greater than shown.

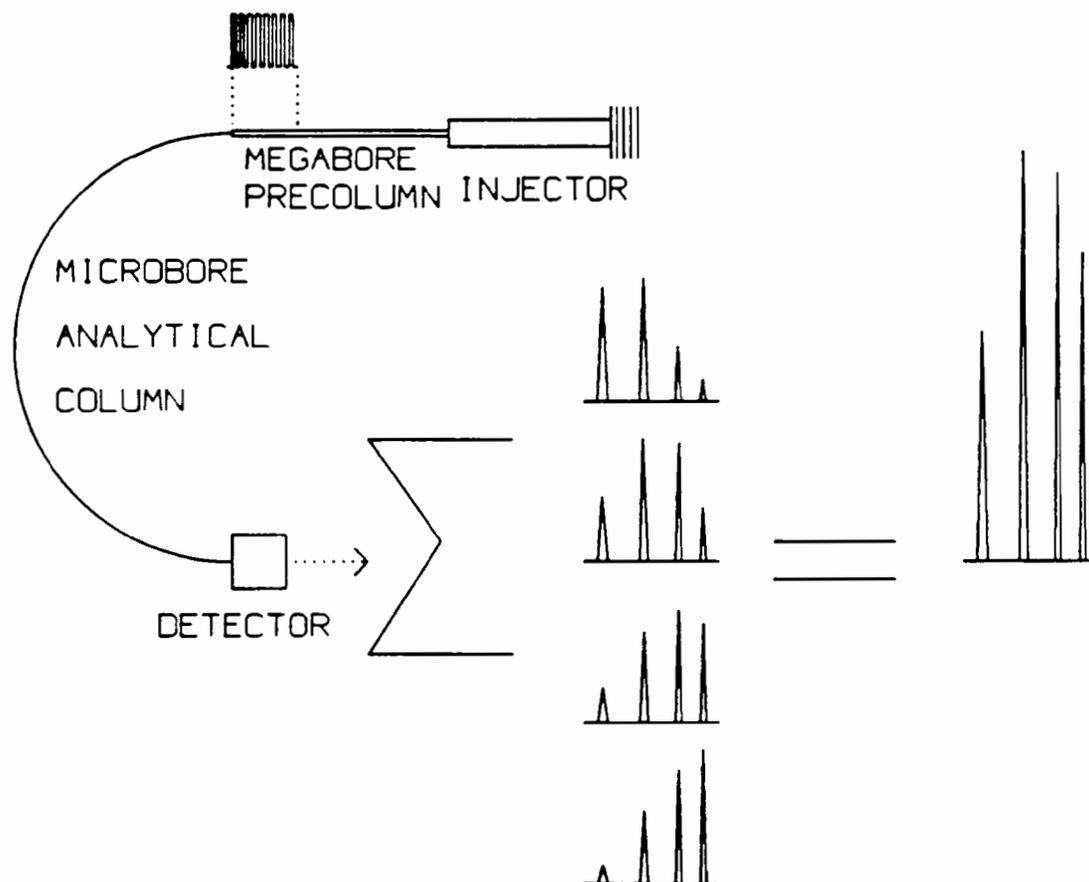


Figure 2. Schematic drawing of a large volume injection into a microbore capillary column showing four representative microchromatograms and the sum of them. The number of microchromatograms is actually much larger. Not taken from actual data.

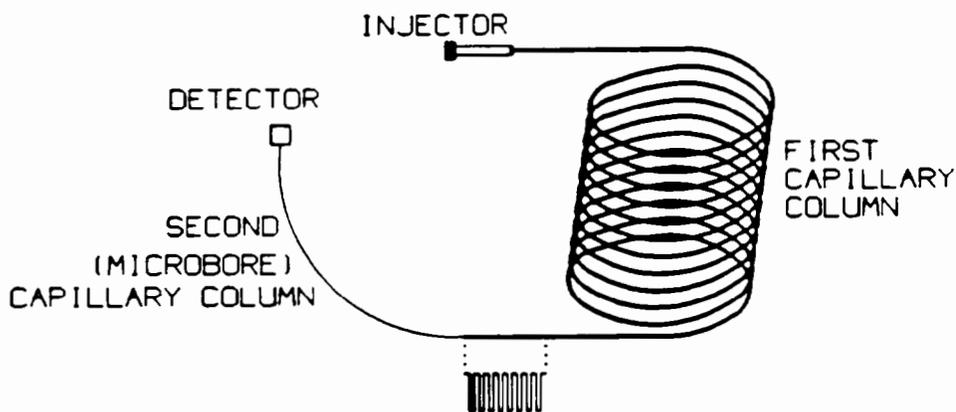


Figure 3. Schematic diagram showing use of peak modulation to produce a two-dimensional chromatogram.

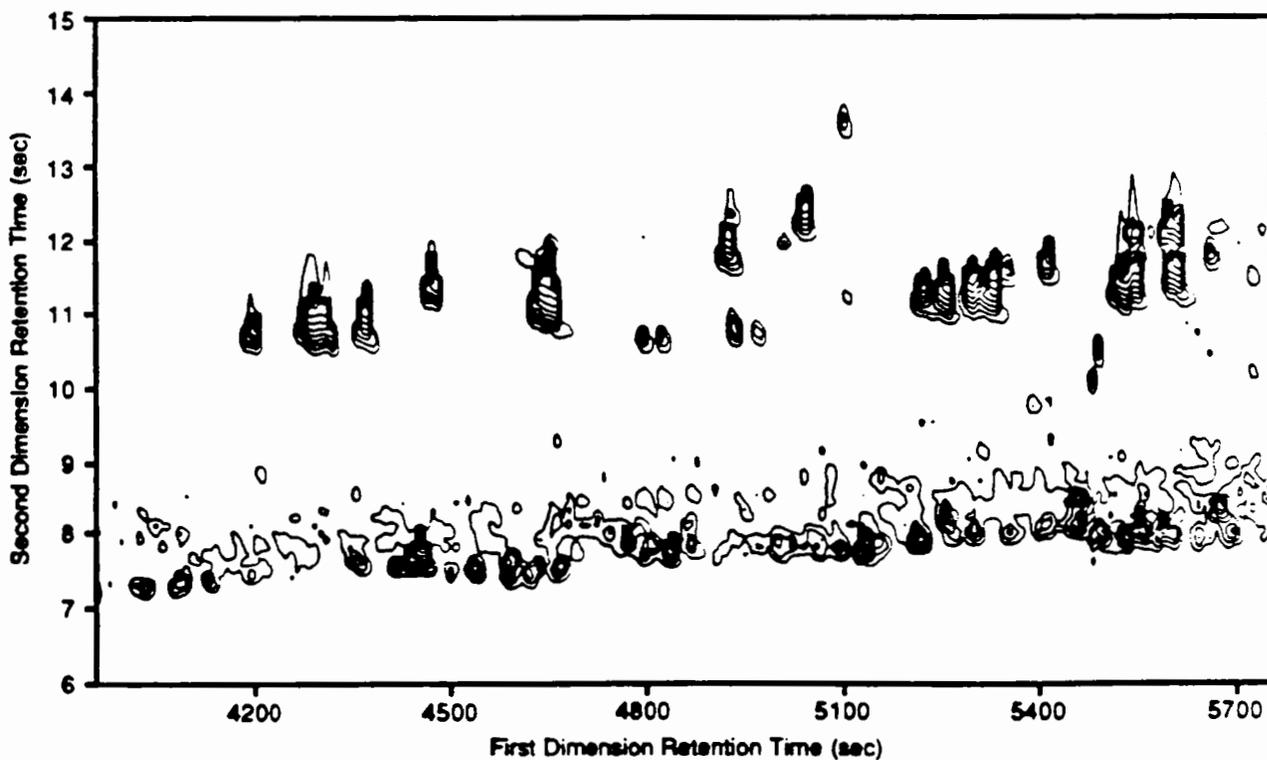


Figure 4. Section of a two-dimensional chromatogram produced by peak modulation [10]. Peaks are seen from above.

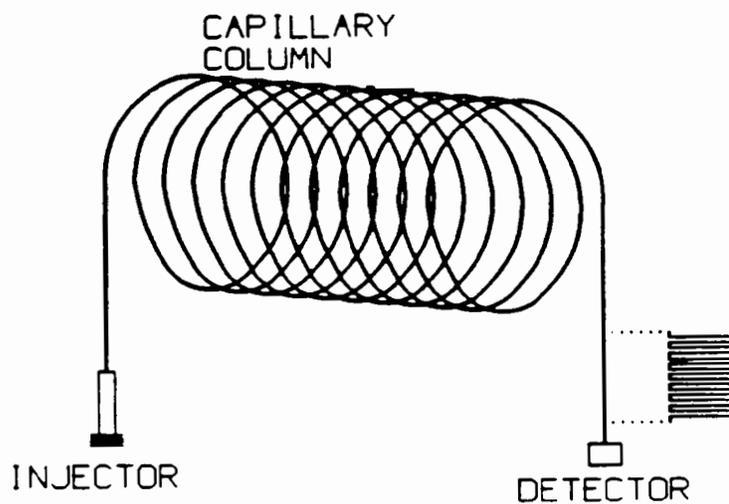


Figure 5. Schematic diagram showing use of modulation to enhance late-eluting peaks.

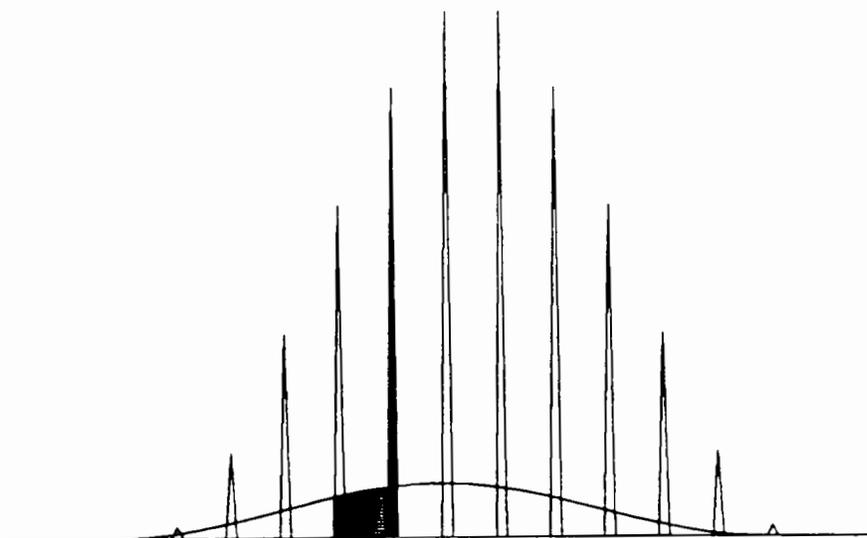


Figure 6. The effect on a late-eluting peak of a peak modulator placed just before the detector. The shaded area of the original peak forms the dark enhanced peak. This geometric construction is not taken from actual data.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

Volatile organic compounds in ambient air are usually estimated by trapping them from air or collecting whole air samples and returning them to a laboratory for analysis by gas chromatography using selective detection. Data do not appear for several days, during which sample integrity could become compromised. Immediate data can be obtained, and sampling errors minimized, by analyzing with a field-deployable instrument at the time samples are collected. Portable gas chromatographs are available, but they don't fully meet the need for quick, high-quality data under field conditions. Shortcomings include insensitive detectors, non-selective detectors, poor resolution, retention time drift, maladroit data processing schemes, excessive energy consumption, and vulnerability to weather. Improved waterproofing, temperature regulation, and energy efficiency are particularly crucial to true field-deployability. Such improvements are probably feasible. Mass spectrometric detection, high-speed chromatography, polycapillary chromatography, and peak modulation may lead to useful enhancements in future.

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