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DEVELOPMENT OF REAL-TIME STACK-GAS ANALYSIS METHODS*

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Summary

Modern analytical chemistry has provided the capability to identify and measure extremely small amounts (10^{-8} to 10^{-10} grams) of specific compounds in a variety of sample types. For organic compounds, these analyses involve primarily separation with high-resolution capillary gas-chromatographic columns and detection of the eluting substances with sensitive detectors such as the flame ionization, electron capture, or, photoionization detector. The analytical capabilities of these instruments are greatly enhanced when eluting compounds are detected and identified with a mass spectrometer. Virtually all of these trace organic analytical procedures involve collection of a sample, transportation of the sample to a suitably equipped laboratory, some sort of extraction of the analytes from the sample matrix and then instrumental analysis of the extract. This entire process provides highly reliable analytical data with appropriate quality control/quality assurance procedures but is quite time consuming and requires the use of a well equipped laboratory. Information on the contents of samples is not available for several days to several weeks.

There is tremendous need for field deployable analytical instruments that can be used on-scene to provide rapid, reliable, cost effective, and timely analysis of organic compounds in a variety of environmental samples and for on-line real-time monitoring of industrial chemical processes. A set of system specifications is given for the optimal performance of such an instrument.

Introduction

Modern analytical chemistry has provided the capability to identify and measure extremely small amounts (10^{-8} to 10^{-10} grams) of specific compounds in a variety of sample types. For organic compounds, these analyses involve primarily separation with high-resolution capillary gas-chromatographic columns and detection of the eluting substances with sensitive detectors such as the flame ionization, electron capture, or, photoionization detector. The analytical capabilities of these instruments are greatly enhanced when eluting compounds are detected and identified with a mass spectrometer. This

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latter technique, commonly known as gas chromatography–mass spectrometry (GC-MS), has the advantage that eluting compounds need not be completely separated from interferences in order to achieve positive identification and accurate quantitations. Virtually all of these trace organic analytical procedures involve collection of a sample, transportation of the sample to a suitably equipped laboratory, some sort of extraction of the analytes from the sample matrix and then instrumental analysis of the extract. This entire process provides highly reliable analytical data with appropriate quality control/quality assurance (QC/QA) procedures but is quite time consuming and requires the use of a well equipped laboratory. Information on the contents of samples is not available for several days to several weeks.

There is tremendous need for field deployable analytical instruments that can be used on-scene to provide rapid, reliable, cost effective, and timely analysis of organic compounds in a variety of environmental samples and for on-line real-time monitoring of industrial chemical processes. We believe such a field deployable analytical instrument system should have the following capabilities: first, it should have the capability to identify specific analytes in the presence of other organic compounds that are commonly found in environmental samples (i.e. it should be selective); second, the device should be able to detect target compounds selectively at concentrations well below their toxic action levels and perform these analyses rapidly; third, it should be rugged, reliable, transportable, cost effective and have the capability to be used by trained but not necessarily experienced chemists or other field technicians; fourth, the device should have the capability to produce data that are comparable to that obtained from laboratory analysis of the sample.

Field deployable analytical instrument

Design

Figure 1 outlines the basic components of a generic, field usable analytical device. All instruments must have at least three basic components in common. There must be a sample introduction system, a detector, and an input–output device. In general, instruments that have these components are generally designed to either detect a single substance, such as chlorine or carbon monoxide, or to provide nonselective response to a wide variety of compounds such as is the case with the hand held photo and flame ionization detectors. A small process control mass spectrometer or mass spectral leak detector can also be considered as an analytical device that is made up of these three basis components.

If greater analytical capabilities are required, additional components must be added to supplement the three basic components of the field deployable analytical device. For instance, the addition of a separation column can turn a simple ionization detector into a much more analytically powerful gas chro-

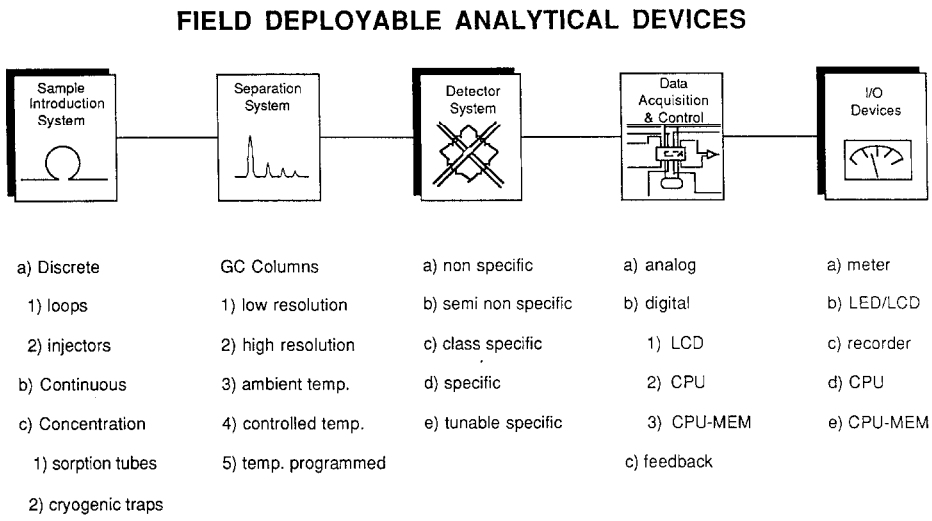

Fig. 1. Outline of a generic analytical device.

matographic instrument. The ability to store and treat raw data will produce a gas chromatograph with enhanced problem solving capabilities. The addition of a mass spectral detector and its associated data system to a gas chromatograph produces an extremely powerful analytical device. It must be emphasized that the capabilities and analytical power of field deployable analytical devices must be matched with their intended uses. Too little analytical capability for the intended task can produce meaningless data while a too sophisticated analytical device is expensive, difficult to operate, and requires a trained operator.

Data handling

Figure 2 is an outline of the steps that are needed to convert an analytical response into useful information. A chemical sensor produces some sort of analytical signal. In the figure, the analytical sensor is a gas chromatograph which separates mixtures of compounds to produce a gas chromatogram (analytical data). The data system changes this analytical data into chemical data such as "benzene detected at 15 ppm". New advances in microcomputers are providing the data handling capability to convert chemical data into useful chemical information that is needed to solve specific problems such as the mitigation of a chemical exposure or control of an incineration process. It must be emphasized that the capability to readily turn analytical data into chemical information requires exceptional analytical reliability from the analytical sensor. Since analytical data are being converted into chemical information without human inspection, the analytical sensor must have the capability to accurately identify and quantitate target compounds and not be influenced to produce "false positive" results from the detection of interfering compounds.

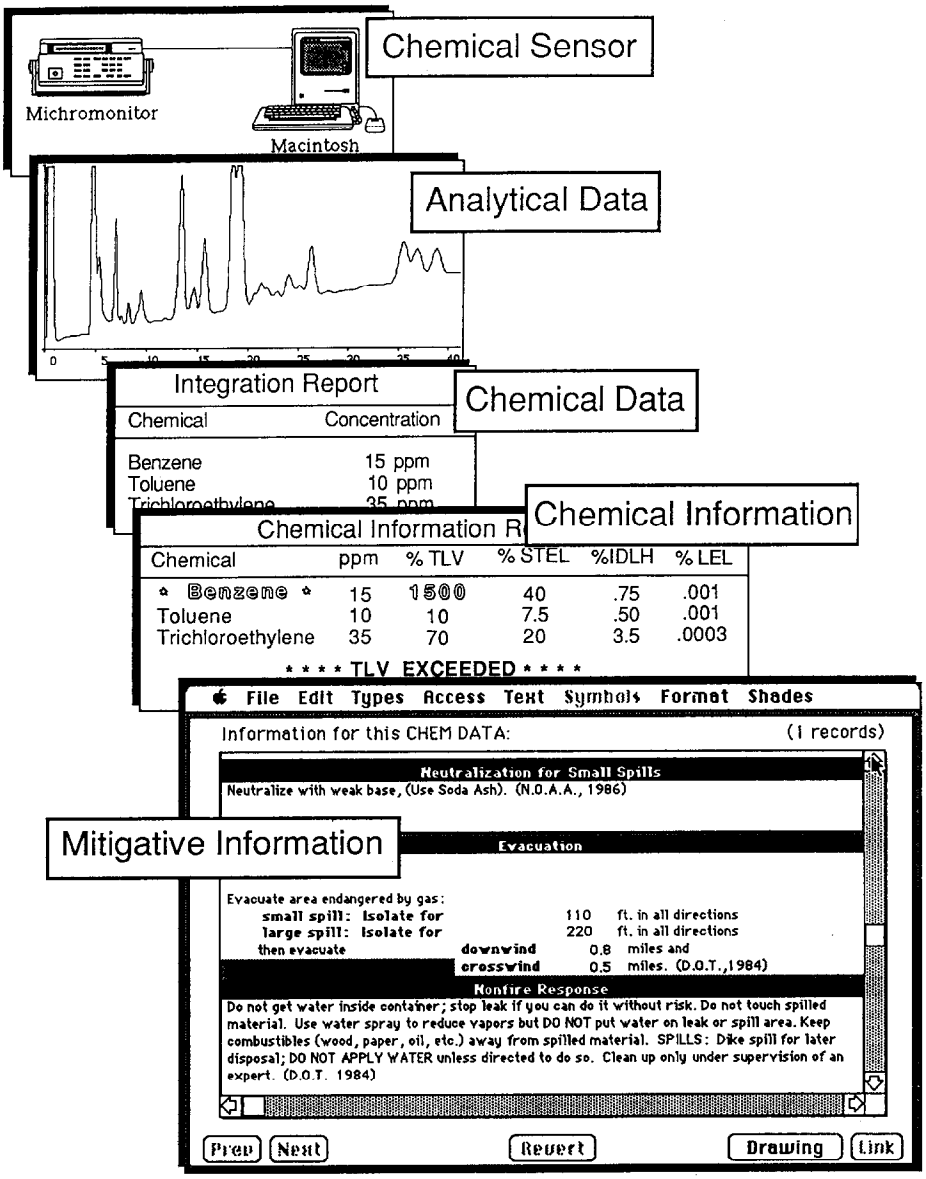

Fig. 2. The steps necessary to convert an analytical signal into useful information.

Consequently, we believe high selectivity is an important attribute for a reliable field deployable analytical device.

Performance

In addition to selectivity, we believe speed is also an important analytical

capability. When monitoring ambient air or the output of an industrial chemical process, a continuous detector is desirable; however, most continuous detectors do not have the ability to separate mixtures, i.e. chromatographic sensors are batch processors, taking discrete samples. The more frequently the samples are taken the closer it approximates a continuous detector, and the speed of an instrument affects how often real-time samples may be taken. While speed and selectivity are of paramount importance, the instrument must, of course, have sensitivity at or below toxic action levels.

Result

We believe a microchip gas chromatograph, the Micromonitor 200 (M200) produced by Microsensor Systems Inc., Freemont, CA, has the attributes to be the sensor element of a highly reliable and useful field deployable analytical device. The M200 is actually two temperature controlled, isothermal, narrow bore capillary gas chromatographs in a single instrument. Each capillary column is coated with a different polarity liquid phase to provide enhanced selectivity while eluting compounds are detected with an extremely small and sensitive but universally responsive thermal conductivity detector. The two microchip gas chromatographs simultaneously analyze air samples on two high resolution narrow bore capillary columns with run times of about one minute. Figure 3 shows data from analyses of standard volatile organic compounds on DB-5 and DB-1701 capillary columns with the M200 instrument. Figure 4 compares the analysis of a soil gas sample with a megabore capillary column using photo ionization detection to that of the M200 narrow bore capillary columns. The speed, resolution, and selectivity of the M200 analysis is readily observed in this comparison.

The M200 does not have any direct output of detector response, and must be linked to an external recording device such as a strip chart recorder or a computer. We have chosen as our recording device the Apple Macintosh personal computer, which may be connected to the M200 via a serial cable. A computer program developed at LSU enables the Macintosh to control the M200, acquire, plot, and integrate the chromatograms, and identify the peaks. The identification algorithm requires that the user run a standard mixture of known compounds to calibrate the instrument. On subsequent analyses the Macintosh will attempt to identify unknown peaks based on a standard library of common pollutants, but the library may be modified to fit a given application. Qualitative analysis is further aided by the use of two chromatographic columns with different stationary phases, which allows the use of correlation chromatographic techniques.

Due to the small amount of sample injected onto the columns the detection limits of the M200 are about 1 ppm (volume/volume). While this level of sensitivity is sufficient for some situations, it is often desired to have detection

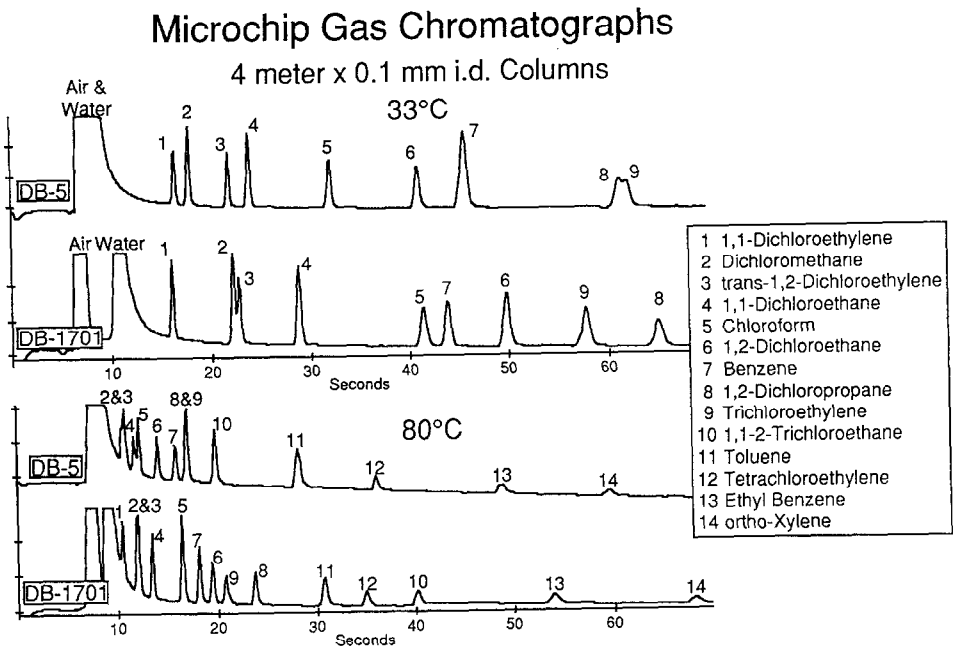

Fig. 3. Speed and resolution of microchip gas chromatographs.

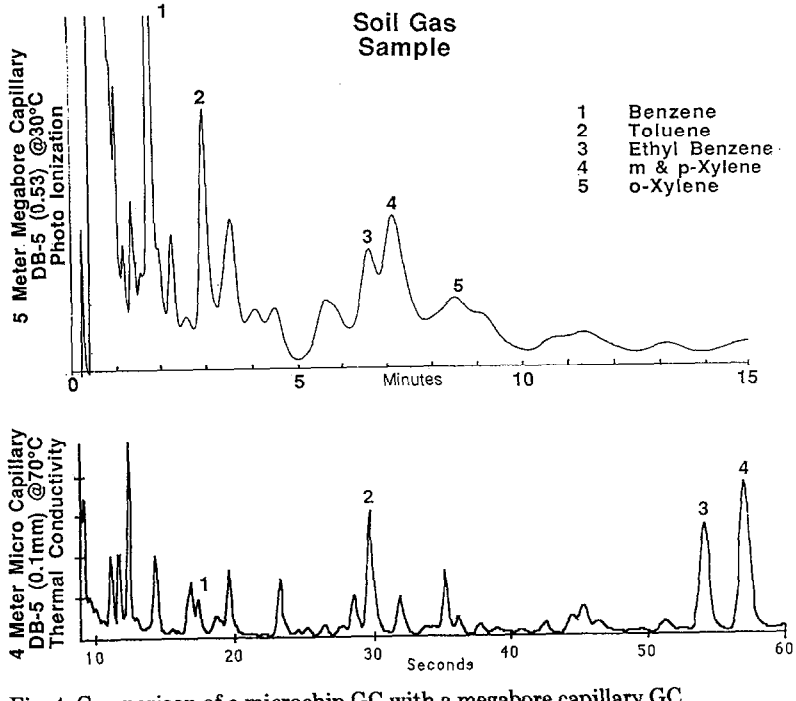

Fig. 4. Comparison of a microchip GC with a megabore capillary GC.

capabilities at or below toxic levels, which can be 1–10 ppb. In order to increase the sensitivity of the M200, a sorption tube sample preconcentrator has been developed. The concentrator, which is shown schematically in Fig. 5, uses two tenax/spherocarb sorption traps to adsorb organic contaminants from ambient air, and thermally desorbs the organics into a smaller volume, thus achieving a "concentration" of the contaminants. The concentrator differs from

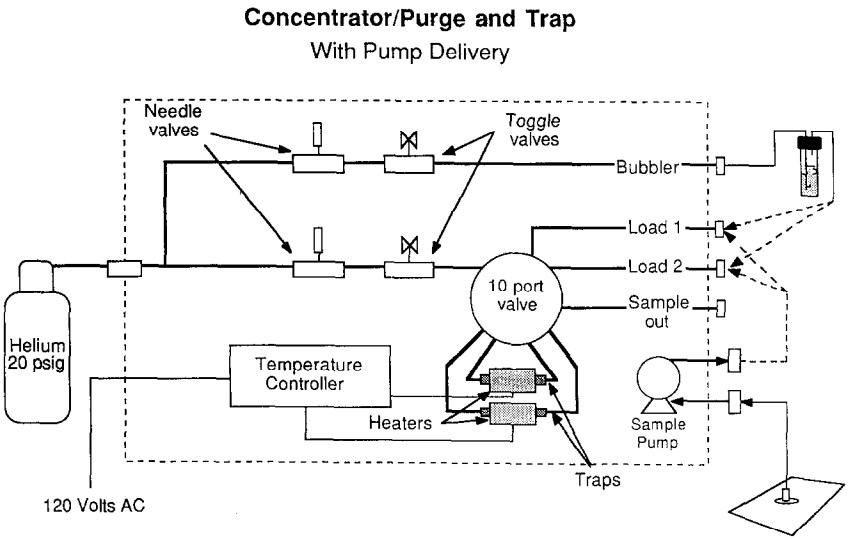

Fig. 5. Schematic diagram of concentrator/purge and trap.

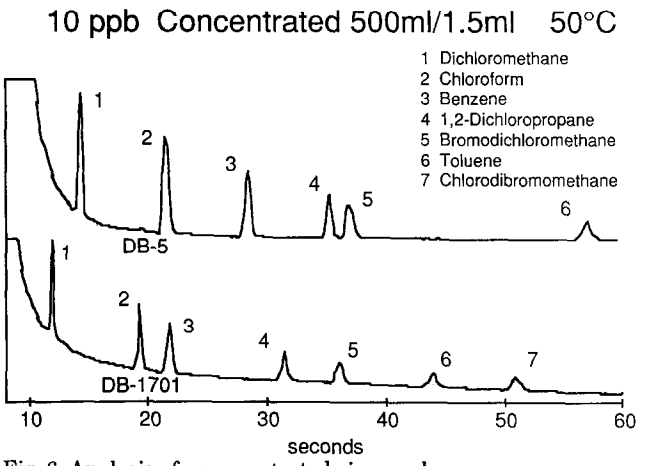

Fig. 6. Analysis of a concentrated air sample.

many other sorption tube devices in that the same traps are used repeatedly, allowing for quality control and reliable recovery data.

The samples are loaded onto the trap via a teflon-diaphragm sample pump. After the trap is loaded, it is heated to 250 °C and the organics on the trap are desorbed into a smaller volume of helium. Concentration factors of up to 500 to 1 have been achieved, as shown in Fig. 6. The concentrator contains two sorption traps in parallel, allowing the operator to load one trap while the other trap is cooling down. This two-trap design allows for nearly continuous operation, and samples may be prepared at a rate of about one every ten minutes. The two-trap design also provides a backup in case one of the traps fails to work properly.

Conclusions

Rapid analysis time, sensitivity, high resolution, and the ability to be taken into the field make the M200 an ideal instrument for the monitoring of continuous industrial processes. Figure 7 shows analyses of the headspace of contaminated groundwater entering and leaving a biological treatment reactor. Such analyses can be performed in real time, and the results can be used for process control and optimization, and to ensure that process effluents are within permitted specifications. The M200 can be set up in an autosampling mode which can analyze samples at set time intervals.

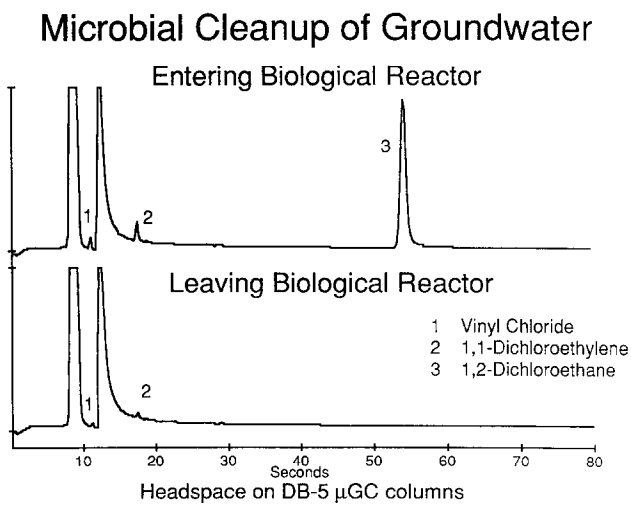

Fig. 7. Analyses of contaminated groundwater entering and leaving a biological reactor.