Sixth Week

Other gas chromatography detectors:

electron capture: halogens, conjugated C=O, —C≡N, $—NO_2$

nitrogen-phosphorus: highlights P, N

flame photometer: individual selected elements, such as P, S, Sn, Pb

photoionization: aromatics, unsaturated compounds

sulfur chemiluminescence: S

nitrogen chemiluminescence: N

atomic emission: most elements (selected individually)

mass spectrometer: most analytes

infrared spectrometer: most analytes

Reactions thought to give sulfur chemiluminescence:

$$\text{sulfur compound} \xrightarrow{H_2\text{–}O_2\ \text{flame}} SO + \text{products}$$

$$SO + O_3 \rightarrow SO_2^* + O_2 \quad (SO_2^* = \text{excited state})$$

$$SO_2^* \rightarrow SO_2 + h\nu$$

ionization detector, excited atoms emit characteristic light. Phosphorus emission at 536 nm or sulfur emission at 394 nm can be isolated by a narrow-band interference filter and detected with a photomultiplier tube.

A *photoionization detector* uses a vacuum ultraviolet source to ionize aromatic and unsaturated compounds; it has little response to saturated hydrocarbons or halocarbons. Electrons produced by the ionization are collected and measured.

A *sulfur chemiluminescence detector* takes exhaust from a flame ionization detector, in which sulfur has been oxidized to SO, and mixes it with ozone (O_3) to form an excited state of SO_2 that emits blue light and ultraviolet radiation. Emission intensity is proportional to the mass of sulfur eluted, regardless of the source, and the response to S is 10^7 times greater than the response to C (Figure 23-20). A *nitrogen chemiluminescence detector* is analogous. Combustion of eluate at 1 800°C converts nitrogen into NO, which reacts with O_3 to create a chemiluminescent product. The response to N is 10^7 times greater than the response to C.

Gas Chromatography–Mass Spectrometry

Mass spectrometry is a sensitive detector that provides both qualitative and quantitative information. With *selected ion monitoring* or *selected reaction monitoring* (Section 21-4), we can measure one component in a complex chromatogram of poorly separated compounds. Selected ion monitoring lowers the detection limit by a factor of 10^2–10^3 compared with *m/z* scanning, because more time is spent just collecting ions of interest in selected ion monitoring.

Figure 23-21 illustrates **selected ion monitoring.** The *reconstructed total ion chromatogram* in trace *a* was obtained from a portable gas chromatograph–mass spectrometer designed for identification of spills at accident sites. A total of 1 072 spectra of eluate were recorded at equal time intervals between 1 and 10 min. The ordinate in the reconstructed total ion chromatogram is the sum of detector signal for all *m/z* above a selected cutoff. It measures everything eluted from the column. The selected ion chromatogram in trace *b* is obtained by parking the detector at *m/z* 78 and only measuring this one mass. By spending all the time measuring just one ion, the signal-to-noise ratio increases and the

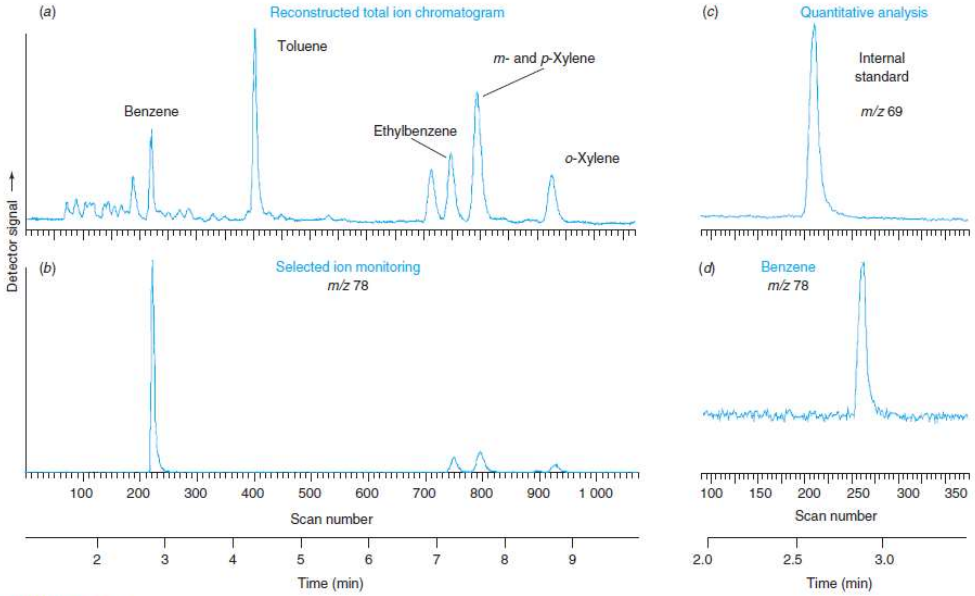

FIGURE 23-21 Selected ion monitoring in gas chromatography–mass spectrometry. (*a*) Reconstructed total ion chromatogram of automobile exhaust with electron ionization. (*b*) Selected ion monitoring at *m/z* 78. (*c*) and (*d*) Quantitative analysis of benzene after adding an internal standard with a prominent ion at *m/z* 69. [Courtesy Inficon, Syracuse, NY.]

chromatogram is simplified. A peak is observed for benzene (nominal mass 78 Da) and minor peaks are observed for benzene derivatives at 7–9 min. For quantitative analysis, an internal standard with a signal at *m/z* 69 is added to the mixture. Even though this internal standard overlaps the congested part of the chromatogram near a retention time of 2 min, the selected ion chromatogram for *m/z* 69 has a single peak in trace *c*. To measure benzene, the area of the *m/z* 78 peak in trace *d* is compared with the area of *m/z* 69 in trace *c*.

Selected reaction monitoring is illustrated in Figure 23-22. Trace *a* is the reconstructed total ion chromatogram of extract from an orange peel. To make the analysis selective for the pesticide fensulfothion, the precursor ion *m/z* 293 selected by mass filter Q1 in Figure 21-26 was passed to collision cell Q2, in which it broke into fragments with a prominent ion at *m/z* 264. Trace *b* in Figure 23-22 shows the detector signal at *m/z* 264 from mass filter Q3. Only

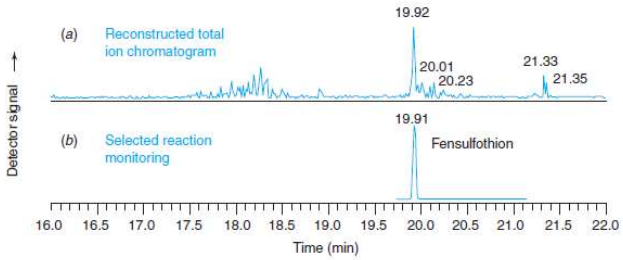

FIGURE 23-22 Selected reaction monitoring in gas chromatography–mass spectrometry. (*a*) Reconstructed total ion chromatogram of extract from orange peel with electron ionization. (*b*) Selected reaction monitoring with the precursor ion *m/z* 293 selected by mass filter Q1 in Figure 21-26 and product ion *m/z* 264 selected by mass filter Q3. The chromatogram is a graph of intensity at *m/z* 264 from Q3 versus time. [Courtesy Thermo Finnigan GC and GC/MS Division, San Jose, CA.]

Element-Specific Plasma Detectors

Eluate from a chromatography column can be passed through a plasma to atomize and ionize its components and measure selected elements by atomic emission spectroscopy or mass spectrometry. An *atomic emission detector* directs eluate through a helium plasma in a microwave cavity. Every element of the periodic table produces characteristic emission that can be detected by a photodiode array polychromator (Figure 19-16). Sensitivity for sulfur can be 10 times better than the sensitivity of a flame photometric detector.

The extremely sensitive inductively coupled plasma–mass spectrometer was described in Section 20-6. Figure 23-23 shows 15 pesticides measured by gas chromatography–inductively coupled plasma–mass spectrometry. Eluate was atomized and ionized in the plasma. Ions were measured by a mass spectrometer that could monitor any set of m/z values. The figure shows traces for P, S, I, Cl, and Br.

23-4 Sample Preparation

Sample preparation is the process of transforming a sample into a form that is suitable for analysis. This process might entail extracting analyte from a complex matrix, *preconcentrating* very dilute analytes to get a concentration high enough to measure, removing or masking interfering species, or chemically transforming (*derivatizing*) analyte into a more convenient or more easily detected form. Chapter 27 addresses sample preparation, so we now describe only techniques that are especially applicable to gas chromatography.

Solid-phase microextraction extracts compounds from liquids, air, or even sludge without using any solvent.[20] The key component is a fused silica fiber coated with a 10- to 100-μm-thick film of stationary phase similar to those used in gas chromatography.

Example of derivatization:

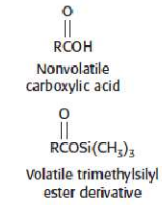

Figure 23-24 shows the fiber attached to the base of a syringe with a fixed metal needle. The fiber can be extended from the needle or retracted inside the needle. Figure 23-25 demonstrates the procedure of exposing the fiber to a sample solution (or the gaseous headspace above the liquid) for a fixed time while stirring and, perhaps, heating. It is best to determine by experiment how much time is required for the fiber to become saturated with analyte and to allow this much time for extraction. If you use shorter times, the concentration of analyte in the fiber is likely to vary from sample to sample. Only a fraction of the analyte in the sample is extracted into the fiber. When you extract the headspace, liquid sample should occupy about two-thirds of the vial. Too much headspace volume reduces extraction efficiency.

After sample collection, retract the fiber and insert the syringe into a gas chromatograph equipped with a 0.7-mm-inner diameter injection port liner. Extend the fiber into the hot injection liner, where analyte is thermally desorbed from the fiber in splitless mode for a fixed time. The narrow port maintains desorbed analyte in a narrow band. Collect desorbed analyte by *cold trapping* (page 578) at the head of the column prior to chromatography. If there will be a long time between sampling and injection, insert the needle into a septum to seal the fiber from the atmosphere. Figure 23-26 shows a chromatogram of chemical warfare nerve agents isolated from seawater by solid-phase microextraction and detected with a nitrogen-phosphorus detector. The chromatogram is deceptively simple because the detector responds only to compounds containing N and P.

In solid-phase microextraction, the mass of analyte (m, μg) absorbed in the coated fiber is

Mass of analyte extracted:

$$m = \frac{KV_f c_0 V_s}{KV_f + V_s} \qquad (23\text{-}3)$$

where V_f is the volume of film on the fiber, V_s is the volume of solution being extracted, and c_0 is the initial concentration (μg/mL) of analyte in the solution being extracted. K is the partition coefficient for solute between the film and the solution: $K = c_f / c_s$, where c_f is the concentration of analyte in the film and c_s is the concentration of analyte in the solution. If you extract a large volume of solution such that $V_s \gg KV_f$, then Equation 23-3 reduces to $m = KV_f c_0$. That is, the mass extracted is proportional to the concentration of analyte in solution. For quantitative analysis, you can construct a calibration curve by extracting known solutions. Alternatively, internal standards and standard additions are both useful for solid-phase microextraction.

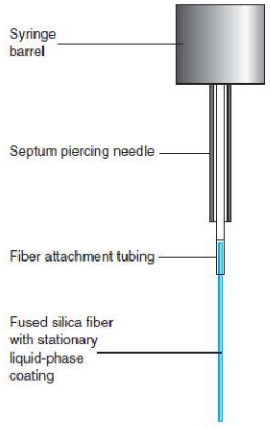

FIGURE 23-24 Syringe for solid-phase microextraction. The fused silica fiber is withdrawn inside the steel needle after sample collection and when the syringe is used to pierce a septum.

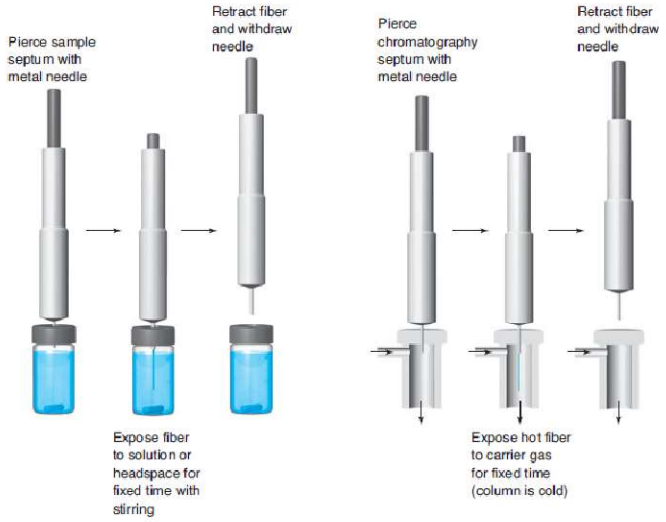

FIGURE 23-25 Sampling by solid-phase microextraction and desorption of analyte from the coated fiber into a gas chromatograph. [Adapted from Supelco Chromatography Products catalog, Bellefonte, PA.]