LABORATORY-BASED ANALYTICAL TECHNOLOGIES

John L. Daniels and Sunyoung Bae
University of North Carolina, Charlotte, North Carolina, USA

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Contents

Summary

This article discusses aspects of laboratory-based analytical technologies used to monitor trace levels of environmental contaminants resulting from the generation and distribution of hazardous waste. Emphasis is placed on contaminants present at trace levels in soil or aqueous phases. The analytical technologies are primarily dichotomized according to whether their prevailing use is for the detection of organic or metal contaminants at trace concentrations. Often, organic contaminants are determined on the basis of chromatographic techniques while metals are analyzed with atomic spectrometry. Mass spectrometry, however, is frequently used in conjunction with a variety of techniques for the analysis of both trace organics and metals.

1. Introduction

Industrial development has led to the generation of hazardous wastes. Such wastes are introduced into the environment at the point of generation as well as through subsequent transportation, treatment, and ultimate disposal. To effectively manage the health risks associated with hazardous waste, the extent of contamination must be quantified in terms of chemical type and concentration. For the purposes of environmental monitoring of the resulting contaminants, the focus is often on determining trace concentrations of organic or inorganic compounds in soil, water, air, and biota. This is accomplished through the application of analytical technologies both at the source of contamination in the field and off-site in a laboratory. The basis for these technologies lies in the broader field of analytical chemistry that has grown tremendously over the past several years in response to industrial, pharmaceutical, and environmental needs. Currently, the major laboratory-based analytical technologies used to determine trace contaminant levels are based on chromatography, atomic spectrometry, and mass spectrometry.

1.1. Laboratory-Based versus Field-Based Technologies

Traditionally, analytical methods and instrumentation required space and resources only available in a laboratory setting. Continued refinements in component design and advances in computer-based data acquisition and control have now allowed for many chemical compounds to be measured on-site where the contamination is of concern. Still, there are advantages and disadvantages associated with either field-based or laboratory-based analyses. Moreover, the current practice of environmental monitoring at hazardous waste sites relies predominantly on laboratory-based analytical technologies with a small, albeit growing use of complimentary field-based efforts.

The use of field-based techniques reduces the time between sampling and analysis and so is more conducive to rapid decision making. However, field-based techniques are typically designed for only specific, limited, chemical compounds while at a typical hazardous waste site there may be myriad contaminants, some which may be unknown at the outset. By contrast, techniques applied in an appropriate environmental laboratory are more equipped to analyze a broad spectrum of chemicals and tend to have lower detection limits. Additionally, many regulators prefer results from laboratories, where established techniques and protocols are followed.

As noted, there is a time lapse between sample measurement and data delivery when an off-site laboratory is used. This delay should be considered with the importance of the data and its prospect for subsequent change as well as the prevailing economics. In terms of media, the temporal and spatial sensitivity increases with intraphase mobility such that air quality indicators may change more quickly than those in water or soil. For example, the results of air monitoring performed to ensure that combustible gases are not present beyond the lower explosive limit are critical for the immediate health of workers in the area of measurement. Such measurements would be conducted with field-based technologies such as a combustible gas indicator with an oxygen meter. Certain environmental contaminants are less likely to change dramatically over the interval of time required for laboratory-based techniques by virtue of their inherent properties and/or the overall matrix. For example, the concentration of heavy metals in soil at a contaminated site is unlikely to change significantly in the time required to make laboratory-based determinations. There may also be direct costs associated with a delay between sampling and analysis. In particular, remedial action often requires the mobilization of equipment and other resources, which may represent a significant portion of a environmental restoration budget. The need for these resources may change on a daily basis in response to results from laboratory analysis.

Because laboratory-based techniques involve a change in time and space, there is the concern for a change in sample integrity. In response to this, elaborate quality assurance and quality control protocols have been established (see *Statistical Analysis and Quality Assurance of Monitoring Data*). These efforts are devoted to documenting the entire process of initial sampling, packaging, transportation, intermediate analyses, and final determination. Moreover, specific procedures have been outlined for dealing with certain contaminants that are subject to change through volatilization, oxidation/reduction, and adsorption onto sampling containers.

In either field-based or laboratory-based analyses, it is critical to obtain samples representative of overall contaminated site conditions. This involves the development of a plan that specifies the timing, frequency, and location for which samples are to be collected (see *Use of Monitoring Data in Human/Ecological Exposure Assessments*).

1.2. Hazardous Waste

Revenues for environmental analytical laboratories derive mainly from hazardous waste management and remediation. Therefore, it is of interest to briefly discuss relevant sources and characteristics of hazardous waste, although a more comprehensive treatment may be found elsewhere .

Hazardous wastes are the consequence of industrial development and, as such, the primary source is derived from commercial manufacturing operations. However, smaller volumes of waste are generated by a large number of other sources including laboratories, hospitals, military installations, gasoline stations, and agricultural operations. Broadly, these wastes may be characterized as either organic or as metals. Within the organic classification, further subdivisions are made for volatile organics, acid-extractable organics, base and neutral organics, pesticides, and polychlorinated

biphenyls (PCBs). By way of example, Table 1 provides a list of selected major priority pollutants.

Volatile Organics	Acid-extractable organics	Base and neutral organics	Pesticides and PCBs	Metals
Acrylonitrile	2-Chlorophenol	Acenaphthene	Aldrin	Antimony
Benzene	2,4-Dichlorophenol	Anthracene	Chlordane	Arsenic
Carbon Tetrachloride	2,4-Dimethylphenol	Benzidene	Dieldrin	Cadmium
Pentachlorophenol	4,6-Dinitro-O-Cresol	Benzo(A)Pyrene	Endrin	Chromium
Ethylbenzene	2-Nitrophenol	4,4'-DDT	Heptachlor	Copper
Methyl Chloride	4-Nitrophenol	Hexachlorobenzene	Arochlor 1016	Lead
Tetrachloroethylene	Parachlorometacresol	Naphthalene	Arochlor-1242	Mercury
Toluene	1,2,4-Trichlorobenzene Phenol	Nitrobenzene	Arochlor-1254	Nickel
Trichloroethylene	2,4,6-Trichlorophenol	Pyrene	Arochlor-1260	Zinc

Table 1. Major priority pollutants

The mode of pollutant introduction to the environment may be a point source as in the discharge of untreated effluent or from nonpoint sources as in runoff from farmland. In either case, contaminants are often dispersed in air, water, or soil at trace concentrations. The term trace should not be taken as negligible considering that low concentrations of certain contaminants may pose serious health risks in terms of the extent to which they are toxic or carcinogenic. It is thus critical to quantify the concentration of a particular contaminant so that appropriate control measures can be taken. A variety of laboratory-based analytical technologies can be used for this purpose and are discussed in the following sections as the focus of this article.

2. Analysis of Trace Organic Contaminants by Chromatography

Applications of chromatography have grown as powerful methods for separation and characterization of complex mixtures. Chromatography is a separation process based on partitioning of sample components between a stationary and a mobile phase. The stationary phase can be either a liquid or a solid while the mobile phase may be a liquid or gas. The mechanisms of separation of sample components can be adsorption, ion exchange, molecular exclusion, and affinity. Table 2 provides a classification of chromatographic techniques.

Mobile phase; classification	Specific method	Stationary phase	Equilibrium mechanism
Gas; Gas Chromatography	Gas-Liquid (GLC)	Liquid adsorbed on a solid	Partition between gas and liquid
	Gas-Solid (GSC)	Solid	Adsorption

(GC)	Gas-bonded phase	Organic species bonded to a solid surface	Partition/adsorption
Liquid; Liquid Chromatography (LC)	Liquid-Liquid (LLC)	Liquid adsorbed on a solid	Partition between immiscible liquids
	Liquid-Solid (LSC)	Solid	Adsorption
	Liquid-Bonded phase (LBC)	Organic species bonded to a solid surface	Partition/adsorption
	Ion-exchange (IEC)	Ion-exchange resin	Ion-exchange
	Gel-permeation (GPC)	Liquid in interstices of a polymeric solid	Partition/sieving

Table 2. Summary of chromatographic methods

Post-column collection and analysis is conducted with a separate analytical technique. A GC or LC is coupled to a discriminating detector such as that used in Fourier transform-infrared spectrometry (FT/IR), ultraviolet/visible spectrometry (UV/Vis), atomic absorption spectrometry, or mass spectrometry (MS). Of these techniques, the use of MS coupled with chromatography is discussed in Sections 4.1 and 4.2.

2.1. Gas Chromatography (GC)

Qualitative and quantitative information can be obtained from a chromatogram and the analysis of retention time, retention plots, and peak heights. These are discussed in turn as follows.

2.1.1. Qualitative GC Analysis

The simplest way to qualitatively identify an unknown compound is to compare the retention time with that of a known component. It is believed that the retention time is characteristic of a substance. Analysis of retention time requires that corresponding volumes as defined by system conditions be calculated as follows:

$$\ln V'_n = a + bn \tag{1}$$

Where:
V'_n = adjusted retention volume, $V_n - V_m$
V_n = retention volume, $t_R F_C$
V_m = hold up volume, $t_M F_C$
t_R = retention time
t_M = hold up time
F_C = flow rate
n = carbon number
a, b = fit parameters

To determine an unknown carbon number for straight chain compounds:

$$x = n_1 + (n_2 - n_1)\frac{\ln V_X - \ln V_{n1}}{\ln V_{n2} - \ln V_{n1}} \tag{2}$$

Where:
V_X = retention volume of unknown compound
V_{n1} = retention volume of known compound 1 with carbon number n_1
V_{n2} = retention volume of known compound 2 with carbon number n_2
x = unknown carbon number such that $n_2 > x > n_1$

Kovat's retention index, l_K, has been used as a parameter for identification of solutes. It is also useful in standardizing results obtained from different instruments and laboratories and is given by:

$$l_K = 100n_1 + 100(n_2 - n_1)\frac{\ln V_X - \ln V_{n1}}{\ln V_{n2} - \ln V_{n1}} \tag{3}$$

One practical approach to analysis unknown compounds is the use of relative retention, given by r:

$$r = \frac{t'_{R(unknown)}}{t'_{R(standard)}} = \frac{V'_{R(unknown)}}{V'_{R(standard)}} \tag{4}$$

The use of relative retention from Eq. (4) is the most common approach, which it only requires a single standard. This standard should be a part of the sample or added to it, in which case it is called an internal standard. It should have characteristics that it elutes near the center of an analysis in terms of retention time. Observed values should remain reasonably constant between runs. However, if compounds too similar to the standard are present, then there is the risk of component misidentification because the differences among retention times are less.

Retention plots are also useful in the qualitative analysis of chromatographic data. Retention values of materials in a homologous series can usually be related to physical characteristics. In many cases, a semilog plot of t_R versus carbon number of the compound may give a linear relationship for the earlier-eluting members of a series. This can be used to identify potential members of the series and to provide a good match with the addition of standards. This type of analysis can be further developed through altering the solvent to change the elution times selectively and/or shift the order of appearance. Such mobile phase changes are possible with liquid chromatography (LC), discussed in greater detail in Section 2.2, however, not with gas chromatography.

2.1.2. Quantitative GC Analysis

Detectors generally produce a measurable response per unit change in concentrations. This is substance-dependent and so a standard must always be used. There are several

ways to obtain quantitative data, including analysis of the peak height/area and use of an internal standard.

The peak height may be determined from a chromatogram by connecting the two sides of the peak with a straight line and then measuring the perpendicular distance between this line and the peak. Such measurements tend to be accurate provided that GC capillary column conditions such as sample injection rate, eluent flow rate and column temperature, are reasonably steady and uniform over the time period of interest. Then, it can be assumed that peak height is proportional to the concentration of compound. This method is attractive because of its simplicity and ease of calculation. However, the height of a peak is more variable than its area.

The area of a peak is unaffected by broadening effects and is therefore a better analytical metric than peak height. Newer instruments are often equipped with an automatic peak integrator, however if none is available then a manual measurement must be made. A simple approximation of the peak area may be made by multiplying the peak height by the width at one-half the peak height. This peak area is also proportional to sample concentration and may be expressed as:

$$C_u = \frac{A_u}{A_k} C_k \tag{5}$$

Where:
C_u = unknown concentration
C_k = known concentration
A_u = unknown area of peak
A_k = known area of peak

Overall, the most reliable approach to quantitative analysis is the internal standard method. A known substance is added at a constant concentration to all standards and samples. Since the internal standard is always present at a constant amount, it can be used to account for variations such as injection volume and rate during an analysis. The internal standard must be carefully chosen so that peaks are separated completely. It is commonly introduced through three ways; by weighing portions of the standard and sample combined, by spiking a known volume of the sample with a known volume of the standard, or by a series of standards being run and a curve plotted based on corrected peak areas. After introduction of an internal standard, the ratio of analyte peak area or height to internal standard peak area or height is used for the calibration plots.

2.1.3. Principles of Operation

GC works best with volatile organic compounds having vapor pressures exceeding 60 torr, boiling points less than 500 ^{o}C, and molecular weights less than 500. In GC, the sample is vaporized and injected into a heated column where separation takes place. The equilibrium between solutes (i.e., components of the sample) carried in the gaseous phase and the sorbent of the stationary phase, is established as the solutes are carried through the column. The various affinity-level of the solutes for the sorbent results in different elution times for the individual sample components. Once separation is

achieved on the column, a detector provides a record of compound separation in the form of a chromatogram. Its signal is plotted as a function of time in order of solute arrival. Solutes that have a low affinity to the stationary phase arrive first on the chromatogram while solutes those are retained longer are eluted. The relative peak positions on the time axis is used to identify the components of the sample while the area under the peaks is used for quantitative analysis as discussed in Section 2.1.2.

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Biographical Sketches

John Daniels is an Assistant Professor in the Department of Civil Engineering and a Faculty Associate in the Global Institute for Energy and Environmental Systems at the University of North Carolina at Charlotte, USA. Recent research has included improvement of barrier material resistance to freeze-thaw and desiccation stress with aqueous polymer solutions, funded in part by the U.S. Army Corps of Engineers Cold Regions Research and Engineering Laboratory and the Clay Minerals Society. He has also worked on research funded by the DuPont Company to enhance the heavy metal attenuation capacity of slurry wall materials. Other research interests include improving the efficiency of geothermal energy extraction through assessment of soil thermal conductivity.

His professional activities include membership with the American Society of Civil Engineers, National Society of Professional Engineers, Solid Waste Association of North America, and Clay Minerals Society. He has worked for TRC Environmental Corporation, Lowell, MA as a project engineer and is a registered professional engineer (PE) in the Commonwealth of Massachusetts and the State of North Carolina. He holds a Bachelor of Science degree in Civil Engineering from Lehigh University, Bethlehem, PA; a Master of Science degree in Civil Engineering and a Doctor of Engineering degree in Civil Engineering from the University of Massachusetts, Lowell, MA.

Sunyoung Bae is the postdoc-fellow at the Global Institute for Energy and Environmental Systems in the University of North Carolina-Charlotte. Recently, she has completed a Ph.D. in chemistry (Environmental Studies Option) from University of Massachusetts-Lowell. During her academic years, she was a teaching assistant and part-time instructor in chemistry, and research assistant at the Biotechnology Center at Tufts University, and at the Center for Environmental Engineering, Science and Technology at the University of Massachusetts. Her activities have focused on physico-chemical interactions between soils and polymer solutions, soil stabilization for dust control, degradation of aqueous polymers from soils, and erosion control. She has proficiency in instrumental analysis such as various spectroscopy, chromatography, nuclear magnetic resonance, and so on. She is a member of the American Chemical Society, Korean-Women Scientist Associate in USA, and Korean Chemical Society.