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Practical Organic Analytical Chemistry for Hazardous Waste Site Investigations

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This chapter describes briefly the analytical techniques used by chemists in analyzing hazardous waste samples. The emphasis is placed on organic compounds because in the vast majority of cases they pose the main threat to aquifers. The main techniques described are **GC/MS**, GC, and **HPLC** with a mention of more novel hyphenated techniques. Because most hydrogeologists and environmental engineers use the services of contract laboratories for their analytical needs, the relationship with laboratories and the need for strict **quality control** is also emphasized. Finally, a case study is described where the perceived problem rested entirely on analytical chemistry for its resolution.

Terms set in boldface type are defined in the Glossary at the end of the chapter.

I. INTRODUCTION

Many treatises have been written on the topic of aqueous analytical chemistry, but most of them are far too comprehensive for the user of analytical results, or are silent on how to interpret analytical data produced by others.

Unfortunately, most laboratory clients—hydrogeologists and environmental engineers—do not understand the jargon of analytical chemistry.

Most introductory courses are long on nomenclature and short on the practical information needed by groundwater contamination investigators. This chapter approaches nomenclature in a different way: just know enough to distinguish between compounds and to recognize synonyms. We hope it will also furnish insight into the behavior of a component in the subsurface of a waste site. Finally, it provides advice on field methods of sampling, preservation, and analysis.

The analytical chemical techniques are not described for the operator of analytical instruments, but more from the viewpoint of the user of the results. Therefore emphasis is placed on the output and on understanding the different levels of confidence that can be attached to laboratory reports. The largest problems usually arise not from what is written down, but from what is not. Assumptions are often the source of misunderstandings; the quality of the client's interaction with laboratory personnel is often key to the success of a groundwater investigation.

An example of a field investigation is described to illustrate the importance of adequate analysis in hazardous waste investigations.

II. LABORATORY SELECTION

Most hydrogeologists have to deal with a contract laboratory when investigating a site. How can one choose a laboratory? This section describes a few indicators that may be used in the selection of a laboratory that will answer specific needs of the hazardous waste site investigator.

A. Interaction with Laboratory Personnel

Although suitable analytical instrumentation and adequate facilities are obviously essential components of a successful laboratory, the personnel will often make the difference between an average facility and a superior facility. It is important to be able to discuss the sampling program with the managers, identify specific needs, and be satisfied that the laboratory personnel will be attentive to them. It should be possible to meet the personnel or at least be informed of which individuals will be involved and what their qualifications (both academic and experiential) are.

The laboratory should have examples of their reports, be willing to do a **blind sample**, and share their **round-robin** results. A protocol should be established ahead of time to deal with unexpected problems, such as loss of samples or nonattainment of quality control criteria, which are possibly due to **matrix effects** but may also be due to the laboratory. Will a second analysis be performed at no extra cost to the client? A comprehensive discussion with several laboratory managers prior to awarding the contract is therefore the first step in any site investigation. It is important to remember that groundwater sampling is expensive and that there often are time constraints that preclude resampling.

B. How Long Will It Take for the Samples To Be Processed?

The best laboratories are often the busiest. It is therefore important to discuss with the laboratory managers how your samples fit into their schedule and what priorities they will receive. Will the laboratory managers take a contract with penalties for late reports, or do they charge a premium for short turnaround times? If there is no provision for timeliness, you must decide whether fast service is important enough for you to look elsewhere.

Many analytical procedures prescribe a maximum allowable storage time for the samples. It is important to be aware of such requirements and to make sure the laboratory respects them. Because the holding time for volatile organic materials is shorter than for semivolatile extracts, the results for **volatiles** should be available more rapidly than for extractable semivolatiles. The laboratory may choose to send you all the results in a final report. If that isn't suitable to you, it should be possible to receive results as they are being produced.

C. Number of Significant Figures Reported

The number of significant figures reported should reflect the **precision** of the analysis. The basic premise of the degree of precision of an analytical procedure is that the results are only as precise as the least precise measurement during that procedure. For most organic analyses, that measurement is either the volume of the sample, measured in the highly imprecise graduated cylinder, the final volume of solvent for the extract, or the amount injected into the analytical instrument—for example, 1 μL in a 10-μL syringe. If the measurement is carried out manually, the best operators claim 5% error; on the average, 10–15% is probably closer to reality. Modern autosamplers can do better, but the flaw is then usually in the measurement of the volume of the final extract, 1 mL by pipette or syringe.

Therefore, the next time you see on a lab report benzene = 5.245 μg/L, use this as a mental flag, and raise the question of the number of significant figures with the chemist. Inexperienced analysts have a tendency to report to the client all the digits printed out by integrators, without considering the meaning of these numbers. If an inordinate number of significant figures are being reported, the instrument output probably received very little review.

D. Professional References

To find a suitable laboratory, as for any other professional service, ask other users for their opinion. It is also very acceptable to ask the laboratory to provide a list of their satisfied clients. This doesn't constitute complete assurance, because laboratory performance can fluctuate. Summer is, of course, a critical period; the sample load increases, regular staff take their annual leave, and summer students learn how to do their first extraction. This is why **QA/QC** has to be an ongoing, integrated process for any investigation. For certain critical investigations, it is possible to request that the same group handle all your samples. A well-run analytical laboratory should be able to integrate new personnel without a decline in performance. The user can ensure him/herself of this continued quality by the application of a rigorous **quality assurance**/quality control program as discussed in Section VI.

E. Suggested Reading

In his book *Quality Assurance of Chemical Measurements*, J.K. Taylor [1] devotes an entire chapter to the issue of laboratory selection.

III. SELECTION OF ANALYTES

The selection of **analytes** in a hazardous waste investigation can be very difficult. At some sites, little or no information is available as to the quantities and types of wastes involved; however, as Plumb shows in Chapter 7 of this volume, volatile organic chemicals are frequently present at hazardous waste sites and it is relatively inexpensive to measure them. If information is available, it often has to be translated into single components. For example, a "total coal tar" analysis is viewed as impossible. However, most laboratories are able to analyze for the components of coal tar, such as benzene, toluene, the xylenes, and the polynuclear aromatic hydrocarbons (**PAHs**). This is why, in this section, nomenclature is discussed before analytes.

A. Nomenclature

Most hydrogeologists have a relatively good background in inorganic chemistry and know which metals and ions are expected to be found in the subsurface. Also, the nomenclature of inorganic compounds is relatively simple because the use of trivial names was discontinued a long time ago; for example, hydrochloric acid is now seldom referred to as muriatic acid. Therefore, only the topic of organic chemical nomenclature is discussed here.

Organic compounds are compounds based on carbon. Additional elements that may be present in naturally occurring organic compounds, in order of abundance, are hydrogen, oxygen, nitrogen, and sulfur. There are a multitude of naturally occurring organic compounds that contain some or all of these elements in combination, and an equally astounding number of synthetic ones. In synthesis, halogens (F, Cl, Br, I) are most commonly added.

For the hydrogeologist, knowing the name of the chemical is not as important as being able to predict its behavior in the subsurface. Therefore, the first thing to do when confronted with a new name is to find out the corresponding structure, because it contains information that will allow the prediction of the chemical's mobility and solubility. Where can this information be found? It can be requested from the chemist who reported the data. Alternatively, it can be found in a number of handbooks such as the *CRC Handbook* [2], *Groundwater Chemicals Desk Reference* [3], the *Merck Index* [4], or even the Aldrich Chemical Company catalog [5]. The use of **CAS numbers** is a good way to ensure that the same compound is referred to.

Compounds that have only C and H atoms are called hydrocarbons. Of all the organic compounds, they are the least soluble in water. They can be saturated or unsaturated, aliphatic or aromatic. Aliphatic compounds have chains of carbon atoms that may be branched or even cyclic. *Saturated* means that carbon is bonded to four different atoms. *Unsaturated* means that two adjoining atoms share more than one pair of electrons and form a so-called double bond. If several unsaturated carbons are linked in a cyclic structure in which the electrons may be shared over several carbons, the compound is *aromatic*. The term *aromatic* comes from the fact that certain hydrocarbons do have a pleasant odor; for example, benzene, toluene, the xylenes, and naphthalene fall into this category. All these compounds are cyclic, and this special configuration of electrons confers more stability. The word *aromatic* should thus be associated with stability. Examples are shown in Fig. 1.

As other atoms such as oxygen, nitrogen, and sulfur are added to the hydrocarbons, their solubility in water increases. Indeed, to be solubilized, molecules have to form weak hydrogen bonds with water. The more similar a compound is to water, the greater is its the solubility. For example, ethanol CH_3CH_2OH) is more soluble than ethane (CH_3CH_3), and in turn ethylene glycol (or 1,2-dihydroxyethane; CH_2OHCH_2OH) is more soluble than ethanol.

Often, students claim that they do not understand organic chemical nomenclature. One problem is the coexistence of several nomenclature systems. This most often arises in connection with biological molecules, whose structures are often too complex to describe simply in chemical terms. It is not hard to imagine what **IUPAC** nomenclature would produce for a protein with a molecular weight of 2000.

As it is easier to learn chemical names and structures if they can be associated with a problem, the wisest learning technique is to look up names and structures as you meet them. Grouping them according to structure is also

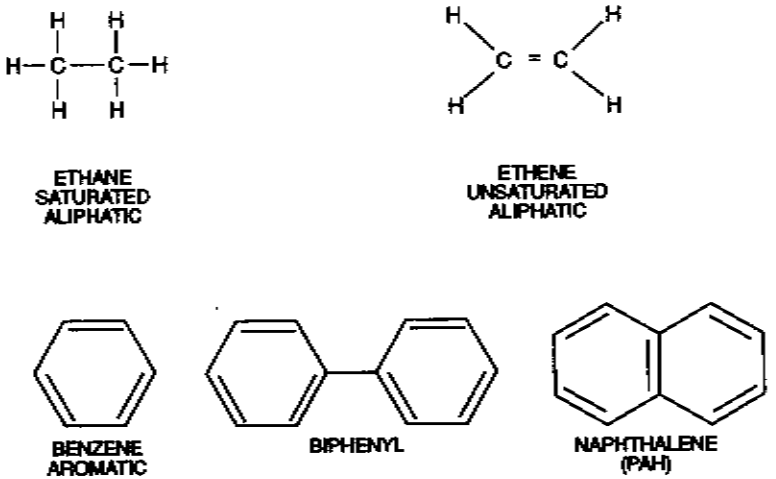

Figure 1 Examples of hydrocarbons.

helpful. For instance, polychlorinated biphenyls are a group of biphenyls (Fig. 1) that differ only in the number of hydrogens that have been substituted by chlorine atoms and thus have similar properties. Polynuclear aromatic hydrocarbons (PAHs) are aromatic compounds that simply differ by the number of fused aromatic rings (rings that share two or more carbons).

B. Target Compound Analysis Vs. Complete Analysis

At the first investigation, the more that can be determined, the better. However, analytical chemistry is expensive, and a rational approach is to be recommended. It has been recognized that the analysis for volatiles can be a very relevant cost-effective technique for assessing groundwater contamination problems [6] (see also Chapter 7, this volume). The reason is very simple: Small molecules are more soluble than their higher molecular weight analog (i.e., methanol is more soluble than octanol), hence they are more likely to have migrated away from the source. Fully automated purge-and-trap systems are found in the vast majority of North American environmental laboratories; alternatively, headspace analysis can be done rapidly. Portable field gas chromatographs (see Chapter 5) are becoming commonplace in hazardous waste site investigations.

Water-miscible compounds, such as acetone, ethanol, acetic acid, 1,4-dioxane, and aniline, are a particular problem. Because of their high solubilities, they are very mobile in the subsurface and are the most likely to move off site, but at the same time the analytical methodologies to address them are often inadequate [7].

Volatiles should therefore be screened in the first analysis, but a more complete analysis should be done closer to the source. Quantitative analysis of U.S. EPA Appendix IX compounds (see Chapter 3, this volume) should be mandatory for selected samples, but it should be remembered that no single list is comprehensive and that most analytical methods are selective. Also, a good proportion of the chemicals found in a typical hazardous site are not on any priority list. There are major difficulties inherent to their measurement, as discussed by Swallow (Chapter 2, this volume). Metal ions should not be neglected, nor should basic field measurements such as pH, Eh, and dissolved oxygen. The problem of selection of parameters is addressed in Part II of this book.

IV. GC/MS ANALYSIS

At the vast majority of hazardous wastes sites, organic chemical analysis is conducted by gas chromatography coupled with mass spectrometry (GC/MS). This is primarily because, although it is relatively expensive, it is the most cost-effective analysis if the amount of information obtained per analytical dollar spent is considered. This section covers the basic principle of GC/MS analysis and its use as both a qualitative and quantitative analytical instrument. Other mass spectrometric techniques are described briefly. The emphasis is placed on the quadrupole instruments because they are currently the most popular in environmental analysis.

A. Trace Organic Analysis

The principle behind most organic analyses is the same and is illustrated in Fig. 2. Compounds dissolved in water are extracted (by a gas for volatiles or a solvent for semivolatiles) and separated by chromatography. Their presence is detected by a detector, the output of which is proportional to the total amount of each component. Quantitation of components is done by integrating the area under the chromatographic peak and comparing it to that of a standard. The specificity of the analysis depends on the type of detector used. It may be relatively nonselective such as the flame ionization detector (FID), where essentially anything that will burn is detected, or fairly specific, such as the electron capture detector (ECD), which will almost only detect halogenated compounds. A mass spectrometer can be used as both a nonselective and a specific detector.

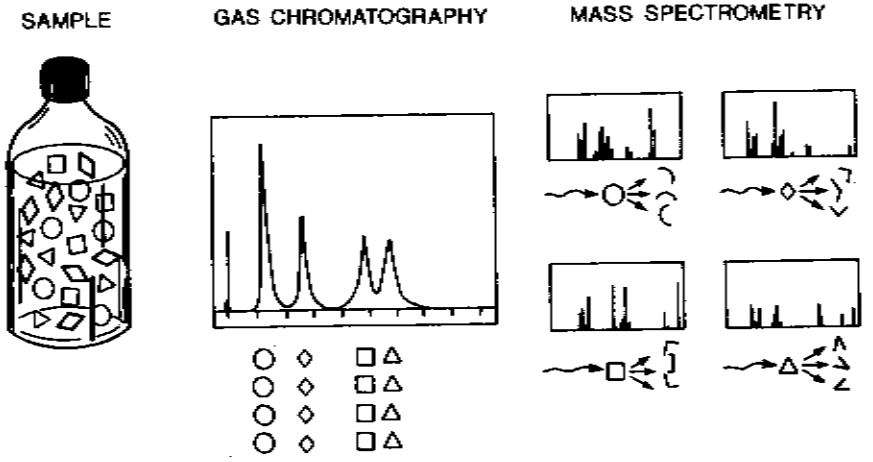

Figure 2 Components of a GC/MS system. (Reprinted from Swallow et al. [8].)

B. Basic Principle

A mass spectrometer is an instrument that differentiates compounds according to their mass. It is composed of three main parts: the ionization chamber, a mass filter (magnetic field or electronic mass filter), and a signal amplifier (electron multiplier). The compound enters the ionization chamber and is bombarded by a current of electrons at 70 eV in a vacuum. This causes the molecule to lose an electron and acquire a positive charge (z). The charged molecule is then destabilized and tends to break down into several smaller fragments along its weakest bonds. These ionic fragments will be attracted to the detector that is of the opposite charge. In a quadrupole instrument the ionized particles travel through a set of four rods (two negative and two positive), to which dc voltages are applied, which act as an electrostatic filter. The ratio mass/z transmitted is proportional to the amplitude of the applied radio frequency, which is scanned with time to allow a selected range of ionized molecules to reach the electron multiplier. For a more detailed discussion, readers are referred to a publication by Haas and Norwood [9]. The mass/z ratio is representative of the molecular mass of the compounds and is thus usually referred to in atomic mass units (**amu** or daltons).

C. Data Acquisition

Gas chromatography-mass spectrometric analyses can be done in two main modes, full **scan** or selected ion monitoring (**SIM**). In the first mode, a range

of masses (typically 45–450 amu) are acquired at the rate of one scan per second; that is, every second a full mass spectrum is obtained and stored in the computer for later retrieval (Fig. 3). The word scan refers to scanning of the radio-frequency voltages as noted above, in a range proportional to the selected masses. In the selected ion mode, only a group of ions, which are typical fragments of the analytes of concern, are acquired (Fig. 4). The chromatogram will reflect the intensity of only these ions. Because usually a maximum of 10-15 ions are monitored simultaneously, the scan rate—the number of scans per second—can be increased, resulting in an increase in sensitivity. Because only a few masses are acquired, it is not possible to identify unknowns in the sample. Also, in heavily contaminated samples, interferences can cause problems. If a large quantity of analytes are requested, the gains in sensitivity are relatively small, and thus it is preferable to acquire a full scan.

Even when a full spectrum is acquired, quantitative analysis is done on extracted ions (Fig. 5). One ion is selected for each compound for quantitation. Each ion is, in essence, a specific detector. As in any chromatographic analysis, the area under the curve of a specific time window is integrated, then the area of the unknown is compared to that of the standard. In addition, the area of one or two other ions characteristic of the analyte are also integrated and their ratio compared to that of the primary ion; these are termed *qualifying ions* because they allow for qualitative identification of a compound. Under the same operating conditions, the spectrum obtained from a given compound is always the same; hence the ratios of the qualifying ions to the primary ion are constant and, in addition to the retention time, are the criteria that are used to ensure correct identification of the analytes (Fig. 6).

The strength of GC/MS over conventional GC detection is therefore twofold. Quantitation using a selected mass, which is characteristic of the target

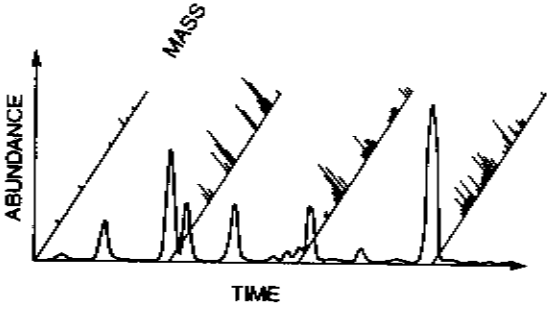

Figure 3 Total ion chromatogram.

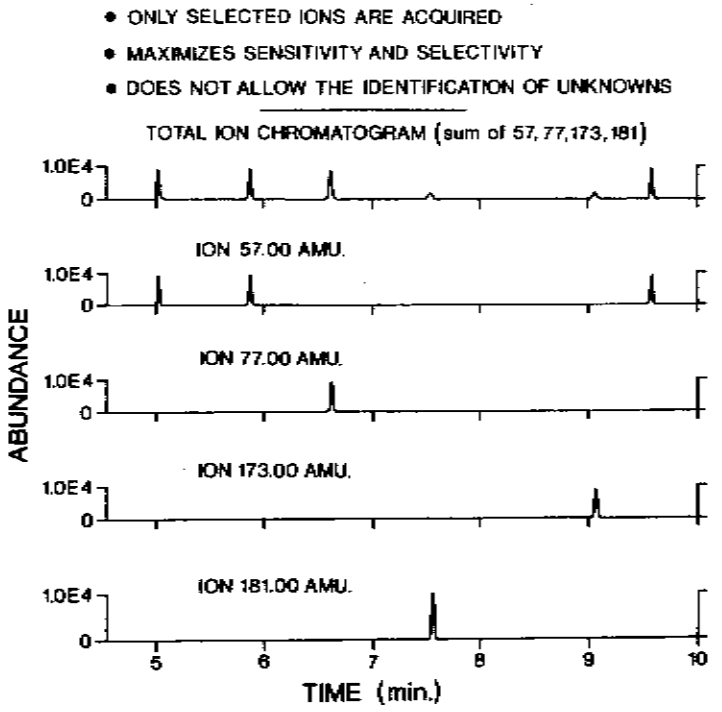

Figure 4 Selected ion monitoring: each channel is a specific detector.

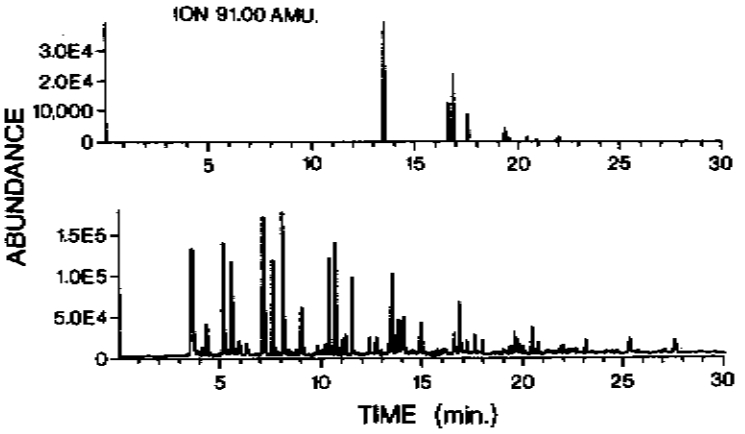

Figure 5 Extracted ion chromatogram: a range of ions (e.g. 45 to 450 a.m.u.) is acquired, but selected ions are quantitated.

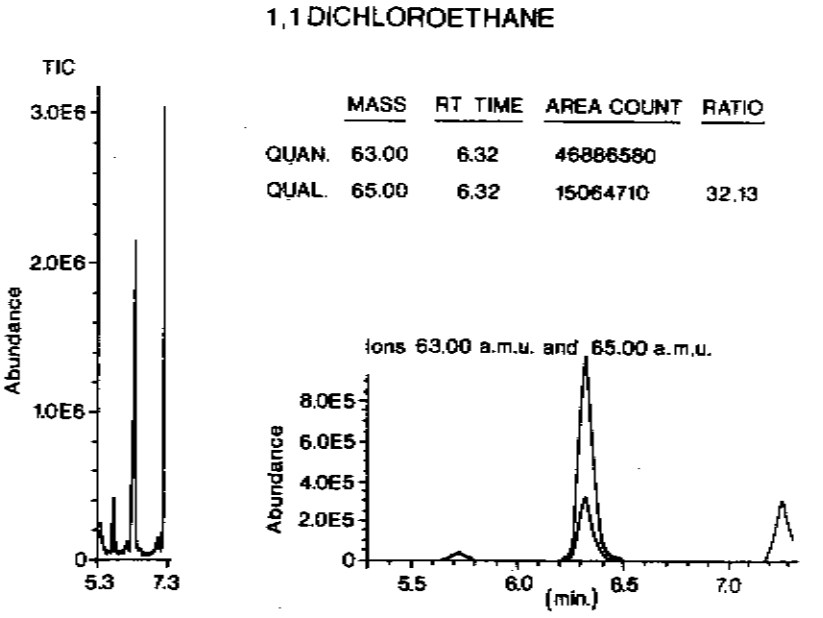

Figure 6 Unknown plus standard quantitation and qualifying ion.

analyte, ensures selectivity and reduces the problem of coeluting interferences. For example, if two peaks were to elute closely, but one is from benzene (mass 78) and the other one from carbon tetrachloride (mass 117), an unspecific detector would see the summed response from the two compounds in the overlapping region. With the mass spectrometer a different chromatogram can be drawn for the two masses in which interference from the coeluting compounds is totally eliminated (Fig. 4). The acquisition of a complete mass spectrum allows for the unambiguous identification of the correct analyte peak and for the tentative identification of peaks arising from nontarget analytes.

D. Library Searches

The identification of the components in a mixture is done by comparing the spectrum of the unknown to that of a library of spectra stored in the GC/MS computer. There are two main methods of doing this comparison: forward search and reverse search (Table 1).

During a *forward search*, the spectrum of the unknown is compared to spectra contained in a library, either a commercially available library such

Table 1 Forward Search Vs. Reserve Search

Forward search
The spectrum of an unknown is recorded.
It is compared to a library of spectra.
A tentative identification is made.
This is the only option available when no standards are available.
Reverse search
A standard is analyzed.
A retention time window and a spectrum are obtained.
Masses characteristic of the compound will be searched in the same retention window.
This is the technique used for quantitative target compound analysis.
It is possible only if a standard is available.
It allows for a much lower detection limit even in complex samples.

as the Wiley library of spectra, which now contains the spectrum of over 100,000 compounds, or a user-created library, which, although usually more modest in size, can be tailored to specific types of compounds and be more efficient. For instance, a pharmaceutical company may wish to use a library containing drugs only. In groundwater analysis, the broader library is the most useful because the contaminants may originate from very diverse sources such as agricultural runoff, industrial spills, and landfill leachates. The output from the search consists of a list of best matches ranked in order of best fit. A perfect match would carry a fit index of 100; this is seldom observed, although matches of 90–95% are not uncommon. When the match is of lesser quality, the chemist must interpret the differences and make a tentative identification. Often the spectrum of the unknown is not present in the library and the library search will give at best an indication of the chemical class of the compound. The mass spectrometer is not very effective at distinguishing between different isomers, because they usually have very similar spectra. Thus, if a series of dimethyl naphthalenes are present in a sample from a wood preservative site, the isomers can be identified only by comparing the spectra with standards.

In a *reverse search*, a group of spectra contained in a user-created library are compared to all the spectra found in a sample. This type of routine is used in target compound analysis. The advantage of reverse search is the ability to identify much smaller quantities of a compound than is possible in a forward search because, even if the peak is of very low intensity or is buried in a group of poorly resolved peaks, it will still be found. This is the type of search that is used in priority pollutant analysis by most laboratories. The danger of restricting oneself to this type of analysis is to miss some nontarget compounds that may be very important. Therefore, whenever a GC/MS scan

is requested from a laboratory, it is essential to clarify whether a forward search will also be carried out to identify "what else may be there." Because forward searches are much more time-consuming, the cost is likely to be higher, but it is the only way to ensure that important constituents are not overlooked. The importance of nonpriority pollutant analysis is also discussed by Swallow in Chapter 2.

E. Problem Samples

Analytical methods are validated for a given analyte or group of analytes in a specific **matrix** (e.g., water, soil, sludge) and for a determined concentration range. When the concentration in the samples falls outside of this range, it becomes necessary to either increase the sample size if the analyte is too dilute, or decrease the sample size when the sample is too heavily contaminated. Either way, this affects the precision and accuracy of the method and should be taken into consideration when evaluating the data.

At many hazardous waste sites, the concentration of one or more analytes often exceeds the working range of methods designed for relatively clean water and soils, and therefore the samples must be diluted. The major effect is, of course, to correspondingly reduce the detection limit of all the analytes present in the samples. Minor constituents will therefore be lost. It is sometimes possible to analyze the sample at two different dilutions, but this will be effective only if the high-concentration contaminants elute relatively far from the analytes present in lower concentrations (i.e., are well separated on the chromatograms). The potential for contamination of the analytical instrument makes this approach impractical. For semivolatile compounds, a liquid chromatographic cleanup can be done on the extract. This fractionates the sample according to chemical classes and is useful only in target compound analysis. For volatiles, no such scheme is possible, because most of the analytes would be lost during processing. It is thus customary to simply dilute the sample with "organic-free" water. Unfortunately, it is virtually impossible to obtain water that is totally free of organic compounds. Also, the polymers used in the traps of the purge-and-trap system are also organic and can bleed small quantities of compounds such as benzene and toluene.

This problem can be corrected by analyzing appropriate **blanks**, but, as there is always a slight variation between analytical runs, there is often a residual amount carried over, usually close to the detection limit. When a sample has been diluted 100-fold, a residual of 0.3 μg/L of benzene will become a reported concentration of 30 μg/L, which may seem significant. In evaluating data arising from diluted samples, it is important to remember to readjust the detection limit and the associated analytical error accordingly. In this case, the detection limit would be 10 μg/L (not 0.1 μg/L). To reflect the actual **accuracy** of the data, it would be best reported as 0.03 mg/L with a detection limit of 0.01 mg/L. Unfortunately, not all analytical

laboratories follow this policy, and the client has to exercise his/her own judgment in evaluating the data.

V. OTHER ORGANIC ANALYTICAL METHODS

As discussed above, GC/MS analysis has a lot to offer because it can provide qualitative and quantitative analysis as well as confirmation of the identity of compounds. It does, however, have limitations. Only compounds that are sufficiently volatile or that can be made volatile through chemical derivatization are amenable to GC/MS analysis. For semivolatile compounds, an extraction is usually done with dichloromethane prior to introducing the sample into the instrument; thus, only extractable compounds are suitable for GC/MS analysis. In environmental samples, this can be as little as 10–15% of the total dissolved organic carbon.

Some samples are sufficiently unstable to warrant immediate on-site analysis. At the moment there are very few portable GC/MS systems that can be brought to the field. Some mobile laboratories have been equipped with mass spectrometers (the Ontario Ministry of the Environment has small vans equipped with **TAGA** systems, a product of Sciex Instruments, Mississauga, Ontario), but in general they are restricted to air sampling where no sample preparation is necessary. Portable gas chromatographs (see Chapter 5) are invaluable tools for field monitoring. Analysis either on-site or close to the site has definite advantages in hazardous waste site investigations, and at the moment this need is best filled with gas chromatography (GC) and high-pressure liquid chromatography (HPLC) (see Chapter 11).

A. Gas Chromatography

Gas chromatographs with specific detectors can outperform GC/MS systems in terms of specificity and detection limit. The electron capture detector was for a long time the sole instrument used by pesticide chemists and is still routinely utilized in analyzing for chlorinated pesticides and PCBs. One of its advantages is its specificity for certain groups of compounds, mostly halogenated hydrocarbons and nitro-substituted compounds. It is also at least 100 times as sensitive as a mass spectrometer, even in the selected ion (SIM) mode. Furthermore, it is much less expensive and thus is a very cost-effective means of analysis. Other commonly used detectors include the flame ionization detector (FID), a good multipurpose detector often used in hydrocarbon analysis; the thermal conductivity (TC) detector, used in gas analysis at the percentage level; the photoionization detector (PID), used mostly for aromatic hydrocarbons but also in portable gas chromatographs such as the Photovac (Thornhill, Ontario); and the nitrogen/phosphorus detector, also

called the alkali flame detector, which is used for pesticide compounds containing nitrogen and phosphorus.

In the gas chromatograph, the separation is done in a column (a tube of glass or metal) filled with a packing material coated with an adsorbent. The separation is based not only on the volatility of the compounds but also on their relative affinity for the packing. Since the early 1980s these columns are being gradually replaced with capillary columns, which provide a much better separation. The most common columns are hollow fused silica tubing coated with a polymeric material. They are typically 30 m in length and have diameters ranging from 0.25 to 0.53 μm.

B. High-Pressure Liquid Chromatography (HPLC)

High-pressure liquid chromatography (HPLC) is the analytical tool of choice for most thermally labile (unstable) compounds. In HPLC, the carrier gas of the gas chromatograph is replaced by a solvent mixture, usually containing a large proportion of water. It is thus quite logical that when the sample matrix is water, HPLC is the instrument of choice. Several detectors have been developed for the liquid chromatographs, the most popular being the ultraviolet, the fluorescence, and, to a lesser extent, the electroconductivity detectors. Ion chromatographs are in essence liquid chromatographs with conductivity detectors. There are two main reasons why HPLC is not used for all analyses: (1) The efficiency of the separation is not as good as what can be achieved with a capillary gas chromatograph and (2) except for the fluorescence detector, the detection systems are not as sensitive, but then, not all molecules fluoresce or can be derivatized to fluorescent species. The derivatization reaction can be carried out postcolumn, that is, following sample elution from the chromatography column. A good example of this in groundwater contamination is the analysis for the pesticide aldicarb and its two toxic metabolites, aldicarb sulfone and aldicarb sulfoxide [10]. The three compounds are separated on the HPLC column and then hydrolyzed and derivatized to the same fluorescent species.

Diode array detectors are now often used in HPLC analysis instead of ultraviolet detectors (UV). They are scanning UV detectors and can provide conformatory data for HPLC analysis in the same way the mass spectrometer does for the gas chromatograph. A UV spectrum is not nearly as useful as a mass spectrum in the identification of organic compounds because it is not as detailed, but there are situations where it is the only possible choice. An example of this is the case of a hazardous waste site where the presence of both phenol and aniline was suspected [11]. These two compounds elute very closely in a gas chromatograph. Phenol has a molecular weight (M) of 94, and aniline, one of 93. However, because carbon has both ^{12}C and ^{13}C

isotopes, there is always a significant $M + 1$ peak in a mass spectrum of organic compounds. Therefore aniline also had a peak at 94. The fragment ions are also similar, which means that mass spectrometry is useless in telling them apart. Aniline also interferes with the total phenols measurement by the 4-aminoantipyrene colorimetric test. The two compounds also elute closely in HPLC, but their UV spectra are sufficiently different that it is possible to distinguish them by diode array detection (Fig. 7).

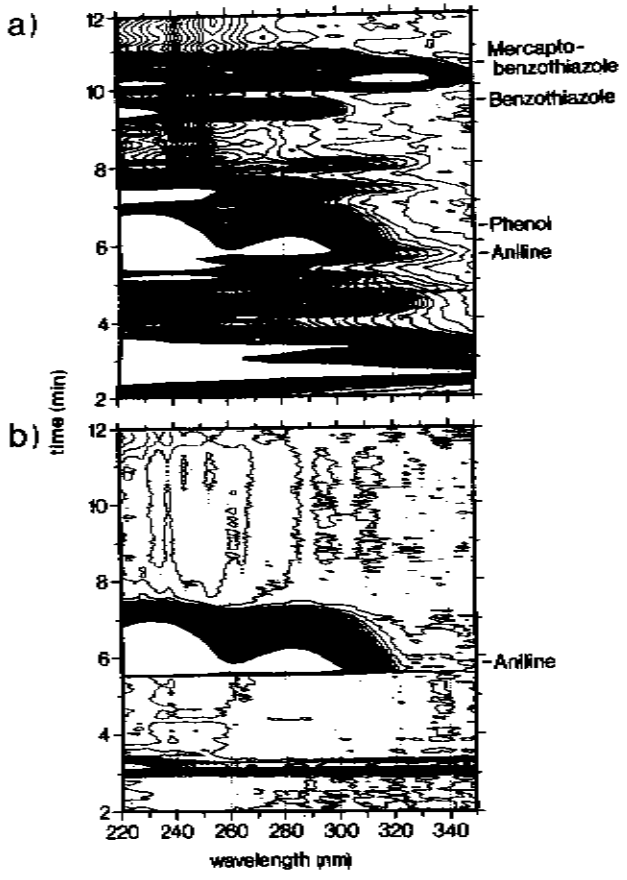

Figure 7 Diode array spectra: Top view, contour. (a) Contaminated groundwater sample: phenol is seen as a peak (lightly shaded area) at 6.8 min and 260 nm. (b) Aniline standard: elutes at 6 minutes.

C. Other Hyphenated Methods

There are also liquid chromatography-mass spectrometry (LC/MS) instruments on the market, but they are not nearly as widespread as GC/MS systems, partly because they are more recent. Indeed, interfacing a liquid chromatograph with a mass spectrometer is a significantly more difficult task than coupling a gas chromatograph to a mass spectrometer. The spectrometer needs to operate in a vacuum, whereas the LC effluent is a solvent, mostly water, mixed with buffer salts. Many ingenious interfaces have been devised, but there is invariably a trade-off in terms of sensitivity [12].

There are several other hyphenated instrumental methods of analysis now available on the market. Most of these are not accepted in regulatory methods because they are either too scarce or still considered too experimental. One of these promising tools is **GC/FT/IR** [13,14]. The GC/FT/IR instrument, which gathers infrared spectra instead of mass spectra, is an excellent complementary tool to GC/MS. It addresses the same range of compounds, but the spectrum obtained gives information on the functional groups of the molecule. For instance, with IR spectrometry it is very easy to distinguish alcohols from ketones and esters. It is also possible to distinguish between **isomers**, for example, between *ortho-*, *meta-*, and *para*-xylenes.

GC/MS/MS systems are used to distinguish between very similar compounds by allowing the analyst to get the mass spectrum of one spectral peak of the first mass spectrum. These instruments contain three quadrupoles in series, operating as magnetic/electrostatic/magnetic fields (B/E/B configuration). The molecule in the ion source fragments along its most vulnerable bonds first, and these are separated by the first quadrupole. The second quadrupole acts as a second ionization chamber and further fragments the molecule. These fragments, also called daughter ions, are then separated by the third quadrupole and detected as in the simple mass spectrometer. This is useful in the case where similar molecules have initial fragments of the same mass/charge ratio. However, when these initial fragments are isolated and bombarded a second time, the secondary fragments will differentiate them. The first mass spectrometer can be tuned to allow compounds of only a certain molecular weight to reach the second mass spectrometer. In effect, it acts as an electronic cleanup system.

VI. QUALITY ASSURANCE/QUALITY CONTROL

The term quality assurance/quality control (QA/QC) finds its way into most analytical contracts, yet a little probing showed that it means different things to different people. The often heard statement "We sent duplicate samples to another lab and their results are different than yours. Why? " summarizes

the frequent failure of what is assumed to be QA/QC by many inexperienced investigators. At that point, there is very little that can be done to salvage the data. The best approach is to design the QA/QC program before the first sample is taken.

A. Definition

The importance of a quality assurance/quality control program is being increasingly recognized, primarily through the efforts of the U.S. Environmental Protection Agency (EPA) [15], which laid out precise guidelines for the implementation of QA/QC for the validation of analytical data. Unfortunately, these have not made their way into the curriculum of most university analytical chemistry courses. Thus, even the meaning of the words quality assurance or quality control is subject to different interpretation. Regardless of how one wants to label them, QA/QC programs need to be operated at two levels. First, within the laboratory, to ensure that good laboratory practice is consistently followed and that the results achieved are of consistent and measurable quality: quality control. This means that, for example, the chemist reporting the results needs to ensure that a concentration of 5.2 μg/L of benzene is accurate (i.e., it wasn't in fact 2 or 10) and that the degree of precision of this measurement (i.e., 5.2 ± 0.2 or 5 ± 1 μg/L) and the detection limit for the sample analyzed can be given to the client. Second, external control by the client has to be implemented to ensure **comparability** of data obtained from different sources and over different time periods. This is called quality assurance and is the responsibility of the site investigator. The sections that follow describe how this can be achieved.

B. Precision and Accuracy

Precision is the degree to which data generated from replicate or repetitive measurements differ from one another [16]. It is obtained by the repetitive analysis of **standards**, to determine the method precision, and of samples, to assess the degree of variation between **replicates.** Any reputable commercial laboratory will provide data on the precision of their analytical methods, but it is the responsibility of the client to request the appropriate number of replicates.

Accuracy is the degree of agreement of a measured value with the true or expected value of the quantity of concern [1]. Accuracy is more difficult to assess than precision but can be evaluated by analyzing certified reference materials and participating in interlaboratory comparisons, also known as round-robins. Certified reference materials, which are generally available from government agencies, are not available for many analytes and matrices, and interlaboratory studies are infrequent. It is possible to get a measure of accuracy by having another laboratory send some **spiked samples** mixed in with the batch of samples submitted.

So, what are the practical tools to ensure that the quality of data obtained meets expectations? Split samples? As stated above, the two main factors that need to be assessed are precision and accuracy; split samples will do neither. If the two data sets agree, it may be fortuitous. If they do not agree, it will not be possible to measure whether the difference falls within normal analytical error or to know which value is the accurate one. The only answer is to prepare a QA/QC program that suits the size and schedule of the sampling program.

C. QA/QC Programs

For large field projects, the regulatory agency will often dictate the QA/QC program. However, for smaller investigations or in countries other than the United States, this task is typically the responsibility of the investigator. An example of an adequate QA/QC program is outlined in Table 1. The total number of QA/QC samples needs to be approximately 10–15% of the total sample load, relatively more if the batch size is small. This includes blanks, replicates, and spiked samples. Blanks should be reported, and it is important to find out whether or not the data were corrected for blanks. Replicates are important because they will be the only measure of sample variability. For this reason, it is preferable to do one sample in triplicate rather than two samples in duplicate. The cost will be the same, but statistical evaluation cannot be done on duplicates. In the example given in Table 2, only three samples were quality assurance samples: the **field blank** and two of the three replicates. This should be sufficient in a batch of 12 samples. The laboratory inserted **reagent blanks** after the standards and after a series of samples to find out about possible carryover. Carryover can occur in certain procedures during which the chemical to be analyzed is adsorbed and then desorbed. If the desorption is not complete, the rest of the compound will be desorbed in the next sample. If this happens to a mixture of standards, it would cause the analyte to be reported in a sample analyzed right after it. The standards were measured at two different concentration levels to allow the construction of a standard response curve (the blank is used for the third data point). This does not always happen in organic analysis because if 50 or more analytes are measured simultaneously, the calculations may be somewhat cumbersome. In that case, a single response factor is measured (area count per unit concentration), and the response of the detector is assumed to be linear.

Spiked samples are used to measure matrix effects and possible bias on the data. This is most important in hazardous waste samples because many

Table 2 Example of a Laboratory Load with Very Good Quality Control

Run no.	Analysis
1	Standard, concentration level 1
2	Standard, concentration level 2
3	Blank (reagent grade water)
4	Sample 1
5	Sample 2
6	Sample 3
7	Sample 4
8	Sample 5 replicate
9	Sample 5 replicate
10	Sample 5 replicate
11	Blank (field or trip)
12	Standard, concentration level 1
13	Standard, concentration level 2
14	Sample 6
15	Sample 7
16	Sample 8
17	Sample 9
18	Sample 10
19	Sample 11
20	Sample 12
21	Blank (reagent)
22	Standard, concentration level 1
23	Standard, concentration level 2

Note: Surrogates are added to all samples.

of the contaminants may be present in high enough concentrations to act as cosolvents and change the composition of the solvent used to extract the analyte from the sample. Indeed, an analytical method developed for water may not be suitable for a concentrated landfill leachate. Unfortunately, unless the expected concentration of the analyte is known ahead of time, it is very difficult for the laboratory to spike the sample at a realistic level.

The matrix effect is measured by comparing the percentage recovery of the spiked compound in the sample with the amount found in distilled water. The percentage recovery of the analyte in the sample is calculated as follows:

$$\text{Recovery (\%)} = \frac{\text{weight}_{\text{spsamp}} - \text{weight}_{\text{ussamp}}}{\text{weight spiked}} \times 100$$

where the subscripts spsamp and ussamp denote spiked sample and unspiked sample, respectively.

In highly contaminated samples for which the analytical error is large, it is not unusual to find more of the analyte in the unspiked sample than in the spiked sample and hence get a negative recovery. For example,

$$\text{Recovery} = \frac{624 \pm 230\ \mu\text{g} - 750 \pm 250\ \mu\text{g}}{100\ \mu\text{g}} \times 100$$

The large standard deviation will often be due to the fact that the sample had to be diluted to stay within the capacity of the chromatographic column and hence is 23 × 10 because of the dilution factor. A standard deviation of 30% is not at all rare for organic analysis. Had the sample not had to be diluted, 100 μg would have been a very realistic spiking range. Unfortunately, only after the sample has been analyzed once is it possible to gauge the appropriate dilution range.

Because the same amount of information can be gathered with one analysis instead of two, and because they are not likely to be found in the samples, spiked samples have been largely replaced by surrogates.

D. Surrogates and Internal Standards

A surrogate is a compound that is an **analog** of the analytes and is added to the sample prior to the extraction step. It can be a deuterated analog (one in which deuterium has replaced hydrogen), most commonly used in GC/MS, or a chemical analog that would not be expected in the samples. It is carried through the entire analytical procedure, and its recovery is reported as a measure of matrix effect and analytical error. The ultimate would be to have a deuterated analog for each analyte (isotope dilution) as described in EPA methods 1624 and 1625 [14], but cost precludes its widespread use.

Surrogates are not to be confused with internal standards. Internal standards are also usually deuterated analogs, but they are added in the final analytical step and are used for quantitative analysis, where their purpose is to account for instrument variability from one sample to the next. The area of the peak of the internal standard in the sample run is compared to the area of the internal standard in the standardization run, and all the concentrations are corrected for any discrepancy.

$$\text{Concentration of } x = \frac{\text{area } x_{\text{samp}}}{\text{area } x_{\text{std}}} \times \frac{\text{area I.S.}_{\text{std}}}{\text{area I.S.}_{\text{samp}}} \times \text{conc } x_{\text{std}}$$

where x denotes the analyte (or parameter), I.S. is internal standard, and the subscripts samp and std denote sample and standardization run, respectively.

It is possible to use more than one internal standard in an analysis to account for the possible behavior of either early- or late-eluting compounds or of acidic or neutral compounds. During purge-and-trap analysis for volatiles, surrogates and internal standards are added together because there is no other preliminary extraction step. Then the only difference between the two is that internal standards are used in the calculations whereas surrogate concentrations are simply reported.

In a typical laboratory report, the percent recovery for surrogates is reported for each sample. Obviously, 100% is the target, but acceptable recovery ranges are much wider, as shown in Table 3.

VII. SAMPLING AND FIELD METHODS

The sampling of contaminated groundwater requires a careful choice of monitoring instruments, the principal criterion of choice being that the individual hydrostratigraphic units within a groundwater flow system must be sampled individually. Wells that penetrate more than a single unit provide little useful information [18,19]. This is because the sample mixing and dilution that occurs in a fully penetrating well imply a greater hydrodynamic dispersion than actually takes place in the aquifer itself. It is also because this integrated (and diluted) sample may indicate contaminant concentrations within the acceptable limits of the guidelines, although these limits may in fact be exceeded within a particular hydrostratigraphic unit.

Figure 8 shows two commonly used devices for sampling groundwater quality: the cluster-type multilevel sampler and the 2-in. (5-cm) i.d. piezometer.

Table 3 Surrogate Spike Recovery Limits for Water and Sediment Samples for Neutral, Acidic, and Volatile Compounds

Surrogate	Water (%)	Sediment (%)
Nitrobenzene-d5	35–114	23–120
2-Fluorobiphenyl	43–116	30–115
p-Terphenyl-d14	33–141	18–137
Phenol-d6	10–94	24–113
2-Fluorophenol	21–100	25–121
2,4,6-Tribromophenol	10–123	19–122
4-Bromofluorobenzene	86–115	74–121
Dibromofluoromethane	86–118	80–120
Toluene-d8	88–110	81–117

Source: U.S. EPA [17].

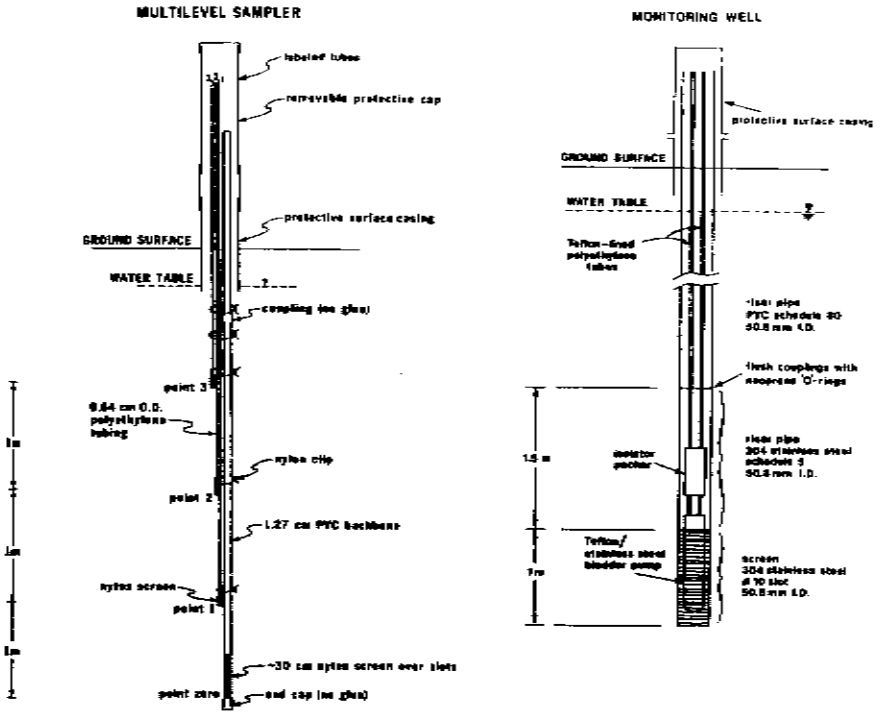

Figure 8 Typical monitoring wells.

Both provide the capability of sampling discrete zones of potentially contaminated groundwater. The first is used to map the outlines of contaminant plumes in three-dimensional details [20]. The second is generally used for monitoring groundwater quality where it is necessary to detect groundwater contamination or to establish that this quality is in compliance with regulated or guideline values. Consequently, the screen material is made of an essentially inert material (e.g., stainless steel). Cowgill [21] presents evidence that the well-casing materials and sampling devices, except those made of PTFE (Teflon), should be steam-cleaned prior to use or installation, respectively.

Samples for detection or compliance monitoring are best collected by using dedicated submersible pumps with PTFE bladders operated by compressed air or nitrogen that does not come into contact with the groundwater sample [22]. The pumps (see Fig. 8) are located at the depth of the well screen and can be isolated from the stagnant water in the well bore by inflating a

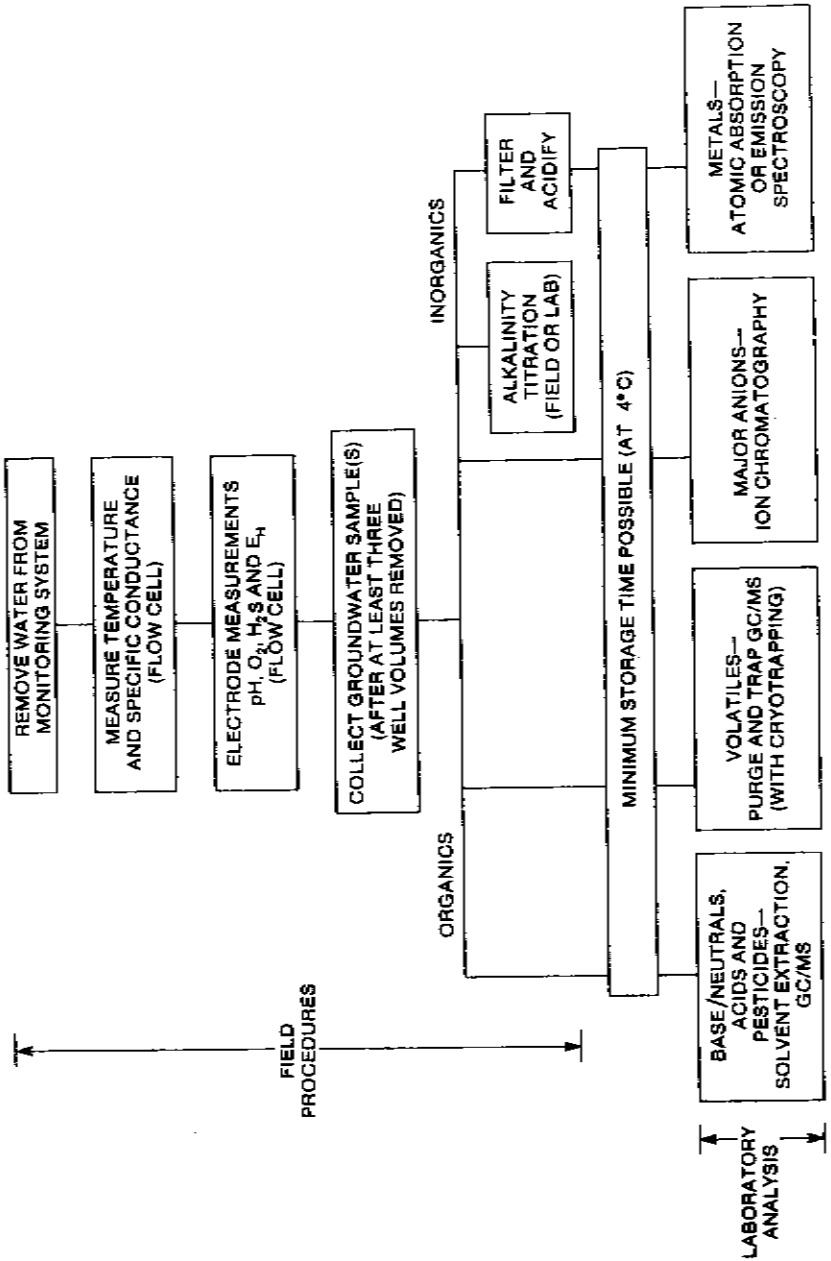

Figure 9 Flowchart for sampling and analysis of groundwater.

packer system, located immediately above the pump. Generally, two or three well-screen volumes of stagnant water are pumped before sampling begins [23,24].

Figure 9 shows a typical sequence of operations conducted in the field to collect samples and the subsequent distribution of aliquots for analytical purposes. Samples are collected in precleaned (and baked) amber glass bottles, with no headspace for volatile organic samples, at a pump delivery rate of 100 mL/min or less. The bottles are allowed to overflow by at least 1.5 volume and are then rapidly capped and stored at about 4°C until analyzed [25]. Sample bottles should not be rinsed out with the sample because a film of organic compounds from any nonaqueous-phase liquids present may adhere to the glass and artificially increase the concentration in the sample.

Measurements of certain unstable constituents—for example, pH, redox potential (Eh), temperature (T), and specific electrical conductance (SEC)—must be conducted in the field. Although referred to as "well purging parameters" [25], in that they are monitored during purging operations and stable readings indicate the appropriate time for sampling, these parameters are critical in the quantitative assessment of water quality [26]. Baedecker and Cozzarelli discuss the collection of groundwaters for dissolved gas analysis, in particular O_2, H_2S, CH_4, NH_3, and CO_2 (i.e., alkalinity), which are critical to understanding the nature of redox processes and metal-ion speciation within the subsurface, in Chapter 14 of this volume.

Preservation techniques for organic constituents of groundwater differ from those for inorganics. In particular, it is inadvisable to subject samples collected for volatile organic analysis to vacuum filtration because of the potential losses by volatilization. Samples for the analysis of volatile aromatic hydrocarbons (e.g., benzene, toluene, ethylbenzene, and xylenes—BTEX) should be preserved with HCl to prevent biodegradation [15]. Inorganic cations are usually filtered and acidified to pH <2 to prevent precipitation or sorption to the container walls, whereas samples for inorganic anions are usually only filtered and refrigerated. Kent and Payne [27] show the importance of the filtration of suspended solids in inorganic analysis and present evidence that frozen icepacks do not adequately chill water samples to 4°C unless the samples are prechilled with wet ice.

Apart from *precision* and *accuracy* (see Section VI.B), groundwater samples must also be *representative* of the hydrostratigraphic formation from which they were collected, *complete* in the sense that the groundwater flow system at the site in question has been fully examined, and, finally, *comparable* with other data collected from the same site. These five attributes define the quality of environmental data and are known as the PARCC attributes [28]. **Representativeness, completeness,** and **comparability** are more the responsibility of the hydrogeologist than of the analytical chemist, who

is responsible for proper precision and accuracy. Good examples of hydrogeochemical studies of hazardous waste sites that observe the PARCC requirements are those of Barcelona et al. [29], Jackson and Patterson [26], and several of the chapters in this book (e.g., Chapters 4 and 11–13). The reader may find more information on groundwater sampling in Reference 25.

VIII. CASE STUDY: NEWCASTLE, NEW BRUNSWICK, CANADA

A. The Problem

This example is taken from the report of a review team composed of hydrogeologists and chemists from WMS Associates, Intera Technologies, and the National Water Research Institute of Canada [30] and was chosen for several reasons. It illustrates clearly the need for strict quality control, it is a good example of how to choose the correct target analytes, and it demonstrates the necessity for hydrogeologists to establish good communication with the analytical laboratory and to include the chemist's viewpoint in the overall assessment of the problem.

The drinking water supply of the town of Newcastle (population 7000) is derived from pumping wells that draw water from a buried-channel sand and gravel aquifer underlying the town. A wood preservation plant that used PCP and creosote for 50–60 years is situated on the outskirts of the town. This plant has been regarded as a potential threat to the municipal water supply, and the plant site is scheduled for cleanup. In the interim, the provincial government has been monitoring the water supply wells for the presence of PAHs, compounds known to be present in creosote and feared because of their toxicity.

In 1988, low levels of PAHs (< 1 μg/L total) were reported to be present in certain wells at certain times. During 1988 and 1989, PAHs were found intermittently during detection monitoring, and both wells were closed in early 1989 because water from them exceeded the 10 ng/L (10 ppt) World Health Organization (WHO) drinking water limit for benzo[α]pyrene. The source of PAH contamination had not been definitively identified, although both the provincial government and the community suspected the wood preservation plant.

Examination of the chemical analysis data revealed a number of QA/QC and other problems:

There was no proper protocol for the sampling and analysis of compounds at or near detection limit or the WHO guideline value of 10 ppt.

No field blanks had been taken to assess the possibility of other sources such as diesel fumes in the pump house or cigarette smoke, and no replicate sample had been analyzed to measure the precision of the data.

The occurrence of the PAHs was sporadic, with different compounds being identified during different sampling rounds, and the more soluble, more mobile compounds present in creosote were not detected together with the PAHs.

The chemist who had reported the data suggesting low-level PAH contamination of the wells had expressed some concern over the validity of his data at the low level of detection requested by the regulators and admitted having had very little experience doing this type of analysis.

The water supply wells used for detection monitoring did not appear to be suitable as monitoring wells with which to establish the level of contamination of the aquifer.

B. The Plan

A complete study was therefore commissioned to determine whether the aquifer was indeed contaminated with PAHs and, if so, to identify the source of the contamination. A survey of the area was conducted to determine all the possible sources of PAHs. Apart from the plant mentioned above, there were several possibilities: a dump site, a small lumber company using wood preservatives, and several potentially leaking fuel storage tanks.

A new set of monitoring wells were drilled with a cable-tool rig (i.e., one needing no compressor or other component producing PAHs), and a rigorous cleaning protocol was followed for the drilling equipment to prevent contamination with any oil or grease. The steel casing was washed with degreasing solvent, detergent, a hot water rinse, acetone, and finally a distilled water rinse prior to use. Samples of the rinse waters were collected and analyzed. Each monitoring well was provided with a dedicated submersible pump to prevent cross-contamination between wells.

Three rounds of sampling were done. The QA/QC program included equipment rinse samples, drill water samples, trip blanks, field blanks, and replicates. The samples were also sent to two laboratories: the one that had published the initial results and a commercial laboratory that was deemed reliable by the review team.

The list of selected analytes was expanded to include, in addition to the PAHs, the volatile organic compounds benzene, toluene, and xylene as well as EPA priority pollutant phenols in order to assess the source of the contaminants. As explained above, the more mobile compounds are the most soluble ones. It was known from studies done by Goerlitz at the USGS (see Chapter 11) that water contaminated by wood preservatives would indeed contain PAHs and that naphthalene would be the predominant species; phenols, mostly methylphenol and dimethylphenol, would also likely be found. From other work [31], it was known that the volatile compounds benzene,

toluene, and xylenes should be also present because they are components of creosote and are even more soluble than naphthalene. Nitrogen-containing heterocyclic compounds should also have been used, but it was impossible to find a commercial laboratory that was immediately able to carry out this analysis quantitatively. Because the city water supply was shut down, bottled water was being used at great expense and inconvenience, and the replacement aquifer supply was still under development, it was important to carry out this project as diligently as possible.

C. The Results

Equipment rinse samples were generally found to contain low levels of phenols and occasionally some PAHs. Drill water samples showed trace levels of phenol (<0.2 μg/L) and cresol, but no PAHs. Distilled water exposed to diesel engine exhaust fumes resulted in low levels of fluorene and phenanthrene (0.17 and 0.29 μg/L, respectively). No PAH was detected in the water exposed to gasoline engine exhaust or to cigarette smoke.

Polynuclear aromatic hydrocarbons were found in two of the three sampling rounds, but the results of the two laboratories did not corroborate each other. One of the laboratories found phenanthrene, fluorene, and fluoranthene, whereas the other found only naphthalene. As with all split samples, this did not tell the reviewing team anything other than that the two labs did not agree. Both laboratories were requested to participate in a round-robin specifically designed to test for the analysis of low levels of PAHs in water, the results of which could be used to assess their capabilities and weaknesses. The next step was to question both laboratories about their procedures to try to explain these discrepancies.

Laboratory 1 did admit to having blank problems at the low level. A close look at their raw data and their procedure showed that although naphthalene was listed on their report sheet, their procedure did not measure it. For them, somehow, "not detected" and "not reported" were equivalent. Their internal quality control was insufficient; they did not add any surrogates to their samples, and the precision of their results could therefore not be assessed. Laboratory 2 used naphthalene-d8 as a surrogate and was reporting constant recoveries for all their samples. They also had a measurable naphthalene concentration in their laboratory blanks. The naphthalene concentration reported for the samples were three times as high. When questioned as to whether they regarded this as significant, they replied affirmatively. Upon further prodding by the review team, they explained that somehow they had not been told in advance that they were expected to analyze for PAHs and phenols and they had to carry out this analysis on 300 mL instead of the usual liter. In the review team's opinion, the naphthalene found in the blank was most likely to be from an impure deuterated surrogate standard. Because the sample size was one-third of normal, this number was multiplied by the dilution factor, 3, which accounted for the apparently significant naphthalene concentration. The dilution factor should have been noted on the laboratory report, but it wasn't.

Was this sufficient evidence to say that the earlier reports were false positives? Probably; but, in addition, no phenols or volatiles were detected in any of the samples. Without the presence of such mobile contaminants in the monitoring well network, the review team suspected that the reported occurrences of PAH "hits" were simply false positives.

D. Conclusion

This very expensive exercise, which cost several million dollars, could have been avoided if the initial sampling had been conducted with proper quality control. The choice of target parameters that are complementary is very important, as no single piece of evidence, even if it is acquired by GC/MS, is sufficient to state a conclusion with certainty. Maintaining a very close dialogue with the analyst and the sampling team is very important for the hydrogeologist, in order for her or him to know whether the samples were effectively collected, shipped, and analyzed.

GLOSSARY

Terms listed in the glossary are set in **boldface** type at first use in text.

Accuracy The amount of bias that a sample may be exposed to during sampling and laboratory analysis [27]; the degree of agreement of a measured value with the true value or expected value of the quantity of concern [1].

amu Atomic mass unit. (1 amu = 1 dalton (Da) = 1/12 mass of one ^{12}C atom.) The mass of a compound calculated from its formula using the lowest mass isotopes expressed in daltons is not to be confused with its molecular weight, which takes isotopic abundances into account.

Analog A compound that differs from another by only a few atoms and thus usually has very similar properties. For example, bromodichlorobenzene is an analog of trichlorobenzene; d-10 anthracene is an analog of anthracene.

Analyte The compound or parameter to be analyzed.

Blanks Samples of the matrix only, used to evaluate possible sources of contamination during sampling and analysis.

Blind sample A sample spiked with a known amount of a standard solution and sent to the laboratory within a batch of samples. Its use helps

to detect any bias or systematic error of the laboratory. However, blind samples are usually very easily spotted by the laboratory because of their unusual mixtures. The same results can be obtained by sending a set of standards.

CAS number In an ultimate attempt to solve the nomenclature problem, the Chemical Abstract Service has come up with a numbering system based on structure. It is an excellent idea to double check the CAS number to ensure that the same chemical is being referred to. One drawback is that very few people can construct a structure from the number. However, structures are easily retrieved from a computer.

Comparability The ability to fairly compare sample test results taken from the same facility at different times [28].

Completeness The number of samples that must be taken and analyzed before a confident judgment can be made that the groundwater conditions at a facility have been adequately assessed [28]; a measure of the amount of data obtained from a measurement process compared to the amount that was expected to be obtained under the conditions of measurement [1].

Field blank A sample of purified water that is transferred to a sample bottle at the same time as the samples are collected, the purpose of which is to ensure that air contaminants are not introduced into the samples at the site. Fuel fumes from pumps and gasoline generators are a common source of problems.

GC/FT/IR Gas chromatography coupled to Fourier-transformed infrared spectrometry. Spectra obtained in the Fourier domain can be easily accumulated; hence this is a method of enhancing the signal from the infrared spectrometer. When coupled to a gas chromatograph, the system can be used in much the same fashion as GC/MS is, with comparison of unknowns with a standardized library of spectra. Infrared spectra allow for the identification of types of functional groups in a molecule (alcohols, amines, ketones, etc.) as well as distinguishing between positional isomers such as *o*- and *m*-xylene).

GC/MS Gas chromatography coupled to mass spectrometry. The gas chromatograph separates mixtures in the gas phase into their components. The mass spectrometer detects them and allows for their quantitation and identification.

HPLC High-pressure liquid chromatography. The HPLC instrument separates mixtures of compounds dissolved in liquids. It is used mostly for aqueous samples and for thermally unstable compounds.

Isomers Compounds that have the same molecular formula (and molecular weight, of course) but in which the functional groups or atoms are arranged differently, giving them different structures.

IUPAC International Union of Pure and Applied Chemistry. This organization has proposed a standardized system of nomenclature.

Matrix The material in which the analyte is dissolved. Water, soil, effluents, landfill leachates, and sludges are typical matrices in environmental analysis.

Matrix effect Interference in the analysis due to interaction between the analyte and the matrix.

PAH Polynuclear aromatic hydrocarbon—one of a group of compounds commonly found in fossil fuels; some have been found to be carcinogenic. The smallest of the group is naphthalene, used in crystal form as mothballs. Benzo[*a*]pyrene is usually the regulated one, with a drinking water limit of 10 ng/L (World Health Organization). Also referred to as polynuclear aromatics (PNAs).

PCP Pentachlorophenol; compound used as a pesticide, mostly as a wood preservative.

Precision The average amount of variability experienced in collecting and analyzing a sample, expressed as the relative standard deviation [28]; the degree to which data generated from replicate or repetitive measurements differ from one another [16].

QA/QC See *Quality assurance* and *Quality control.*

Quality assurance A system of activities whose purpose is to provide the producer or user of a product or a service the assurance that it meets defined standards of quality with a stated level of confidence [1].

Quality control The overall system of activities whose purpose is to control the quality of a product or a service so that it meets the needs of the users. The aim is to provide quality that is satisfactory, adequate, dependable, and economical [1].

Reagent blank An analysis carried out using all the reagents but no sample. It is used to ascertain the purity of the analytical reagents used in a specific method.

Replicate In an experiment, a repeat using the same variables. In analysis, a repeat of the same sample using the same analytical conditions. "Duplicate" means two replicates.

Representativeness A subjective assessment of whether the sample truly reflects the groundwater in a particular hydrogeologic unit at a particular location [28].

Round-robin Interlaboratory study in which a group of laboratories all analyze a subsample from a large homogeneous sample in order to compare their methodology and their accuracy.

Scan In mass spectrometry, a given range of masses (e.g., 50–450 amu or daltons) acquired in a specified time (e.g., 1 sec). In other spectroscopies, the acquisition of a range of wavelengths; for example, an ultraviolet scan refers to the acquisition of an adsorbance spectrum from 200 to 650 nm.

SIM In mass spectrometry, selected ion monitoring. In contrast to the scan mode, only a few masses (e.g., 78,151,153,173) are acquired. This takes only a fraction of a second and allows several acquisitions to be performed in 1 sec, enhancing the sensitivity for these ions. Not to be confused with SIMS.

SIMS Secondary ion mass spectrometry, a technique in which nonvolatile compounds are ionized on a metal surface [9].

Spiked sample A sample to which a known amount of analyte is added to measure the matrix effects on the analytical methodology. A large sample is divided in two; half is spiked, the other half is left intact, and both samples are analyzed in parallel.

Standard A solution of known composition made from the purest available chemical and used to calibrate an instrument for quantitative analysis.

Surrogate A compound that is representative yet different (often deuterated or fluorinated) from the target analytes and is added to the sample prior to extraction. Its recovery is indicative of a matrix effect.

TAGA Target atmospheric gas analyzer, a mass spectrometer with the source at ambient pressure, which allows instant on-site monitoring of atmospheric gases.

Trip blank A sample of laboratory-purified water that travels unopened from and back to the laboratory along with the sample bottles, to find out about possible contamination in transit. See also *field blank*.

Volatiles A group of compounds that can be analyzed by purging them out of water with a stream of inert gas at room temperature. Their boiling point is below 150°C.

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