Environmental Monitoring and the Gas Industry: Program Manager Handbook

Topical Report
June 1990 - October 1997

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RESEARCH SUMMARY

Title Environmental Monitoring and the Gas Industry: Program Manager Handbook

Contractor North Dakota State University

Principal Investigator G.C. Gillispie

Report Period June 1990 to October 1997

Topical Report

Objective To develop a document for nontechnical gas industry management personnel that will provide information for educated decision making in the areas of field sampling, shipping, and analytical methodology applicable to gas industry wastes.

Technical Perspective This report is to aid program managers, administrators, and other persons involved in the decision-making processes who may not be familiar with analytical processes. Its principal goal is to provide background information relevant to chemical analysis as applied to gas industry wastes, thereby assisting managers in their communications with analytical specialists, regulatory agencies, and other concerned parties.

Results This report describes the analytical process from determination of sampling objectives, sampling concerns and steps involved, selection of analytical technique, concepts, terminology, and basic principles. It includes references for further reading and an extensive index for easy search within the document.

Technical Approach The author brought together his experience as lecturer, teacher, and consultant to develop a document which answers questions on sampling and chemical analytical methodology that management needs to ask in order to get the data it needs for decisions involving waste management or site cleanup. Source material was also obtained from the literature, experts in various analytical techniques. Originally a section on groundwater sampling was planned. However, during the literature search a superior document from EPA was found and has been incorporated in this document as an appendix.

Project Implications This document is a handbook for nontechnical managers and regulators who must make decisions based on waste, soil and groundwater sampling, and analytical data. Decisions on handling of chemicals, management of wastes, and cleanup or remediation of soils and groundwater have important economic effects on the oil and gas industry. Many of the decisions are made by nontechnical management people relying on data that could be flawed because of inappropriate sampling or analytical methods. To date, there has been no single source of information on how material should be sampled and
what analytical method is best to use with a particular sample to give the most reliable data on the contaminants of concern. Where such literature exists, it is often written in scientific jargon. This document changes that. The analytical section of the document describes the basic principles of the most common and important analytical techniques/instrumentation and what types of samples they work with best and the information they will deliver, all in straightforward terms familiar to the nontechnical manager or regulator. The sampling portion defines the does and don’ts of soil and groundwater sampling in nontechnical language.

GRI Project Manager
James M. Evans
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<td>AA</td>
<td>Atomic Absorption</td>
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<td>e</td>
<td>Absorptivity</td>
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<td>AE</td>
<td>Atomic Emission</td>
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<td>AED</td>
<td>Atomic Emission Detector</td>
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<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
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<td>AWR</td>
<td>Analytical Working Range</td>
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<tr>
<td>BTEX</td>
<td>Benzene/Toluene/Ethylbenzene/p-Xylene</td>
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<td>BOD</td>
<td>Biological Oxygen Demand</td>
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<tr>
<td>°C</td>
<td>Celsius</td>
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<td>CE</td>
<td>Capillary Electrophoresis</td>
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<tr>
<td>CERCLA</td>
<td>Comprehensive Environmental Response, Compensation, and Liability Act</td>
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<td>CGE</td>
<td>Capillary Gel Electrophoresis</td>
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<td>CIA</td>
<td>Capillary Ion Analysis</td>
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<td>CIEF</td>
<td>Capillary Isoelectric Focusing</td>
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<td>CITP</td>
<td>Capillary Isotachophoresis</td>
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<td>CLP</td>
<td>Contract Laboratory Program</td>
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<td>COD</td>
<td>Chemical Oxygen Demand</td>
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<td>Capillary Zone Electrophoresis</td>
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<td>Diethanolamine</td>
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<td>DEGS</td>
<td>Diethylene Glycol Succinate</td>
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<td>DL</td>
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<td>DQO</td>
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<td>fm</td>
<td>Femtomole</td>
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<td>Flame Photometric Detector</td>
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<td>FPD(P)</td>
<td>Flame Photometric Detector (selective for phosphorus)</td>
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<tr>
<td>FPD(S)</td>
<td>Flame Photometric Detector (selective for sulfur)</td>
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<td>FSOT</td>
<td>Fused Silica, Open Tubular</td>
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<tr>
<td>ft</td>
<td>Foot</td>
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<td>FT-IR</td>
<td>Fourier Transform Infrared</td>
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<td>GC</td>
<td>Gas Chromatography</td>
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<td>Description</td>
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<td>GFAA</td>
<td>Graphite Furnace Atomic Absorption</td>
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<td>HCL</td>
<td>Hollow Cathode Discharge Lamp</td>
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<td>HH</td>
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<td>HHA</td>
<td>Heated Headspace Analysis</td>
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<td>High-Performance Liquid Chromatography</td>
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<td>High-Performance Thin-Layer Chromatography</td>
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<td>IC</td>
<td>Ion-Exchange Chromatography</td>
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<td>ICAP</td>
<td>Inductively Coupled Argon Plasma</td>
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<tr>
<td>ICP</td>
<td>Inductively Coupled Plasma</td>
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<td>Kilovolts</td>
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<td>L</td>
<td>Liter</td>
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<td>Liquid Chromatography</td>
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<td>Laser-Induced Fluorescence</td>
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<td>LLE</td>
<td>Liquid-Liquid Extraction</td>
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<td>LOD</td>
<td>Limits of Detection</td>
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<tr>
<td>LDR</td>
<td>Linear Dynamic Range</td>
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<td>LN</td>
<td>Liquid Nitrogen</td>
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<tr>
<td>M</td>
<td>Molar</td>
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<tr>
<td>MDEA</td>
<td>Methyldiethanolamine</td>
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<td>MEA</td>
<td>Monoethanolamine</td>
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<td>MECC</td>
<td>Miscellar Electrokinetic Capillary Chromatography</td>
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<td>mg</td>
<td>Milligram</td>
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<td>MIP</td>
<td>Microwave-Induced Plasma</td>
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<td>mm</td>
<td>Millimeter</td>
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<td>MS</td>
<td>Mass Spectrometry</td>
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<tr>
<td>MSD</td>
<td>Mass Selective Detector</td>
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<tr>
<td>MTBE</td>
<td>Methyl \textit{Tertiary}-Butyl Ether</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass/Charge</td>
</tr>
<tr>
<td>ng</td>
<td>Nanogram</td>
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<tr>
<td>nL</td>
<td>Nanoliter</td>
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<tr>
<td>nm</td>
<td>Nanometer</td>
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<td>NPC</td>
<td>Normal-Phase Chromatography</td>
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<td>NPD</td>
<td>Nitrogen Phosphorus Detector</td>
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<td>ODS</td>
<td>Octadecyl Column</td>
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<td>OPO</td>
<td>Optical Parametric Oscillators</td>
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<td>OTCs</td>
<td>Open Capillary Tubes</td>
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<tr>
<td>PAH</td>
<td>Polycyclic Aromatic Hydrocarbon</td>
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<tr>
<td>PCB</td>
<td>Polychlorinated Biphenyl</td>
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<tr>
<td>pg</td>
<td>Picogram</td>
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<td>PID</td>
<td>Photoionization Detector</td>
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<tr>
<td>PLOT</td>
<td>Porous Layer, Open Tubular</td>
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<tr>
<td>PMT</td>
<td>Photomultiplier Tube</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>PNA</td>
<td>Polynuclear Aromatic Hydrocarbons</td>
</tr>
<tr>
<td>ppb</td>
<td>Parts per Billion</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per Million</td>
</tr>
<tr>
<td>PT</td>
<td>Purge and Trap</td>
</tr>
<tr>
<td>PVI</td>
<td>Plasma Vacuum Interface</td>
</tr>
<tr>
<td>Q</td>
<td>Charge</td>
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<tr>
<td>QA/QC</td>
<td>Quality Assurance/Quality Control</td>
</tr>
<tr>
<td>QAPP</td>
<td>Quality Assurance Project Plan</td>
</tr>
<tr>
<td>RCRA</td>
<td>Resource Conservation and Recovery Act</td>
</tr>
<tr>
<td>Rf</td>
<td>Radio Frequency</td>
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<td>RIA</td>
<td>Radioimmunoassay</td>
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<tr>
<td>RI</td>
<td>Refractive Index</td>
</tr>
<tr>
<td>RPC</td>
<td>Reverse-Phase Chromatography</td>
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<tr>
<td>RSD</td>
<td>Relative Standard Deviation</td>
</tr>
<tr>
<td>SCIC</td>
<td>Suppressed Conductivity Ion Chromatography</td>
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<tr>
<td>SCOT</td>
<td>Support-Coated, Open Tubular</td>
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<tr>
<td>SEC</td>
<td>Size Exclusion Chromatography</td>
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<tr>
<td>SFE</td>
<td>Supercritical Fluid Extraction</td>
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<td>SHA</td>
<td>Static Headspace Analysis</td>
</tr>
<tr>
<td>S/N</td>
<td>Signal-to-Noise Ratio</td>
</tr>
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<td>SPE</td>
<td>Solid-Phase Extraction</td>
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<td>TCD</td>
<td>Thermal Conductivity Detector</td>
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<tr>
<td>TDS</td>
<td>Total Dissolved Solids</td>
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<td>TFME</td>
<td>Thin-Film Mercury Electrode</td>
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<td>TLC</td>
<td>Thin-Layer Chromatography</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
<tr>
<td>torr</td>
<td>Unit of Pressure</td>
</tr>
<tr>
<td>TPH</td>
<td>Total Petroleum Hydrocarbon</td>
</tr>
<tr>
<td>TRPH</td>
<td>Total Recoverable Petroleum Hydrocarbons</td>
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<td>TSS</td>
<td>Total Suspended Solids</td>
</tr>
<tr>
<td>μL</td>
<td>Microliter</td>
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<tr>
<td>UV/VIS</td>
<td>Ultraviolet/Visible</td>
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<tr>
<td>VOC</td>
<td>Volatile Organic Compound</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength</td>
</tr>
<tr>
<td>WCOT</td>
<td>Wall-Coated, Open Tubular</td>
</tr>
<tr>
<td>XRF</td>
<td>X-Ray Fluorescence</td>
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EXECUTIVE SUMMARY

This document has been developed for the nontechnical gas industry manager who has the responsibility for the development of waste or potentially contaminated soil and groundwater data or must make decisions based on such data for the management or remediation of these materials. It explores the use of common analytical chemistry instrumentation and associated techniques for identification of environmentally hazardous materials. Sufficient detail is given to familiarize the nontechnical reader with the principles behind the operation of each technique. The scope and realm of the techniques and their constituent variations are portrayed through a discussion of crucial details and, where appropriate, the depiction of real-life data.

It is the author’s intention to provide an easily understood handbook for gas industry management. Techniques which determine the presence, composition, and quantification of gas industry wastes are discussed. Greater focus is given to traditional techniques which have been the mainstay of modern analytical benchwork. However, with the continual advancement of instrumental principles and design, several techniques have been included which are likely to receive greater attention in future considerations for waste-related detection. Definitions and concepts inherent to a thorough understanding of the principles common to analytical chemistry are discussed.

It is also crucial that gas industry managers understand the effects of the various actions which take place before, during, and after the actual sampling step. When a series of sample collection, storage, and transport activities occur, new or inexperienced project managers may overlook or misunderstand the importance of the sequence. Each step has an impact on the final results of the measurement process; errors in judgment or decision making can be costly. Specific techniques and methodologies for the collection, storage, and transport of environmental media samples are not described or discussed in detail in this handbook. However, the underlying philosophy regarding the importance of proper collection, storage, and transport practices, as well as pertinent references, are presented.
1.0 INTRODUCTION

The University of North Dakota (UND) Energy & Environmental Research Center (EERC), at the request of Gas Research Institute (GRI) and with the support of both GRI and the U.S. Department of Energy (U.S. DOE), has initiated a long-term research program designed to 1) identify and assess subsurface impacts related to gas industry wastes and 2) use that knowledge to provide the gas industry with the necessary tools (for example, databases, models, characterization protocols and techniques, and remediation technologies) to effectively and economically address these issues. It is hoped that this program will aid the understanding of the tools and techniques that are part of the process. This information is important to the development and understanding of the integrated laboratory and field activities that are fundamental to achieving the program's overall objectives.

The primary products of the research program activities are a series of reports that are often interrelated and that are accompanied by one or more relevant databases. In addition to summarizing information important for focusing future program activities, these reports are designed to provide gas industry managers and environmentally focused gas industry personnel with up-to-date overviews of significant areas of interest, as well as valuable specific data in forms that they can readily use.

In order for gas industry personnel to properly identify and assess the nature of gas industry-related compounds in the subsurface environment, it is critical that they possess at least a basic knowledge of the analytical techniques considered standard and acceptable by environmental scientists and regulators. Literature and other pertinent sources regarding the present state of analytical methodologies applicable to gas industry wastes were reviewed and are discussed in this document. Recommendations concerning appropriate use of analytical methodologies are also included. Proper collection, preservation, pretreatment, and shipping methods are critical for accurate and reliable analysis of soil and groundwater samples. These procedures are discussed and references provided; however, a complete evaluation of their methods is beyond the scope of this report. Supplementary references are provided in Section 12.0. The information provided in this report serves to guide the integrated laboratory and field activities that are fundamental to achieving the research program's overall objectives.

1.1 Objective and Rationale

Understanding and controlling the environmental impacts of day-to-day operations are common tenets among industrial producers. Gas industry wastes are highly regulated at both the state and federal levels. Growing concern for the well-being of our environment is reflected in the nature and degree to which government regulations are applied. The gas industry must make increasingly complex and costly decisions about the environmental impact of its activities. Assessment and remediation of subsurface waste problems must be addressed.
Chemical analysis allows qualitative and quantitative identification and monitoring of environmental impact. The pivotal role of chemical analysis applies not only to current and anticipated activities, but also to past industrial practices. Because of the high cost of chemical analysis, a great deal of importance is placed on speed, accuracy, precision, and economy of environmental analysis. An initial project activity assessed current state-of-the-art analytical methodology applicable to gas industry wastes. This report outlines the results of an assessment of the current state-of-the-art analytical methodologies that are applicable to natural gas industry wastes.

The primary objective of this assessment is to target program managers, administrators, and other policy makers who may lack the chemical and/or analytical training required for knowledgeable decision making and provide these individuals with a readily accessible source of background information regarding chemical analysis as applied to gas industry wastes. With the help of this text, gas industry personnel will have an improved understanding of the processes involved in chemical analysis and will be better able to communicate their situations and needs to chemical labs, specialists and regulatory agencies.

This report specifically addresses situations of greatest relevance to the gas industry. Waste materials of concern to the natural gas industry and the technology used to identify and otherwise analyze those materials are the main portion of the report. Although the extent of future regulated contaminants is not known, those more likely to be regulated are included here.

"A Project Manager's Guide to Requesting and Evaluating Chemical Analyses" (Environmental Protection Agency [EPA] 910/9-90-024) is a document written with similar goals in mind. From the Introduction:

"With each passing year, environmental planning and assessment activities require government agencies, industry, and environmental groups to spend larger and larger amounts of money to analyze the chemical content of water, air, soil, sediment, and tissue samples. The projects for which these samples are analyzed range from small to very large, and the experience of project managers and staff in requesting chemical analyses and in evaluating the resulting data range from essentially none to substantial. For project managers and staff with minimal to average experience in this area, conducting these tasks may be formidable. In fact, a project manager may simply accept laboratory results as definitive with 'no questions asked' or must rely on the expertise of in-house or contracted quality assurance specialists, if available."

The purpose of this manual is to help less-experienced project managers from governmental agencies, industry, and environmental groups in requesting appropriate laboratory services and in making an informed evaluation of the results of chemical analyses. Most managers of environmental projects are not chemists, but many will need to plan for, request, discuss, or evaluate chemical analyses. Even after the results have been returned or interpreted, many managers must still defend the project data or critical decisions made that led to the final results.
The Project Manager's Guide and this document are complementary. We have included analytical techniques and principles in greater detail along with figures illustrating "real-world" data. More specific information is provided on the actual analyses themselves. Finally, this report's contents are not limited to techniques that have already met the criterion of regulatory acceptance by EPA or other governmental agencies. Environmental monitoring is an extremely dynamic area of research and development. In light of the possibilities, we have emphasized developments that may have future significance.

1.2 Approach

Environmental monitoring applications can be categorized by the matrices in which the species of interest may be found. Analytical techniques for groundwater and soil (including soil gas) are given greater emphasis here than is the atmosphere. There is a fourth "environment," that of a process stream, and many of the techniques assessed in this study may be applied to samples collected from the process stream. On-stream analysis also referred to as in situ or real time, could greatly improve operations in the gas industry through increased efficiency of chemical and/or physical manipulations of raw materials and reduction of environmental emissions. As regulatory requirements become more stringent, the economic benefit of such minimization will increase. The efficacy and applicability of on-stream analysis will depend on some of the developing techniques discussed here.

Of concern to some environmental scientists, regulators, and industry managers is that the actual analytical assessment is too much in the forefront, while collection, shipping, preservation, and pretreatment aspects critical to the overall treatment of the sample are often downplayed or ignored. Although specific methods for sample collection, shipment, preservation, and pretreatment are beyond the scope of this report, an understanding of the philosophy behind proper preanalysis activities is important. The goal of any environmental analysis project in the broadest terms is to obtain the most representative samples; to preserve the integrity of samples during shipping, storage, and pretreatment; to accurately analyze for the species of interest; and to accomplish these activities economically while still meeting regulatory acceptance. Successful completion requires accurate communication at many stages between project managers, sampling personnel, chemical analysts, and regulators. There is often little or no overlap between these four groups in terms of training, motivation, and function. The fact that no analyst can overcome the deficiencies of a bad sample has been noted numerous times. Yet far too often, the analyst is isolated even from the decision of where and how to sample. The analyst is simply presented with the sample and asked to test it.

Section 2 focuses on general considerations in regard to sampling and analysis objectives. The need to clearly define project objectives is emphasized. The choice of the sampling and analytical methods depends upon the intended use of the data and hence the data quality objectives (DQOs). A rational choice of the DQOs requires an appreciation for how an analysis can go wrong. Too often perhaps than is justified, there is heavier reliance on the data and trust in the significance of reported data. The actual analysis step lies at the end of a long chain of operations, any area of which can potentially negate the outcome. Section 3 outlines some examples.
Section 4 is a review of analytical concepts and terminology. Key terms along with statistical and other data concepts are defined and, in many cases, illustrated. A major philosophical point brought out in this chapter is that there are trade-offs between cost, speed, accuracy, precision, and other relevant factors. Particular attention is given to the concept of a calibration curve and the factors that affect its use.

Background on the main techniques applicable to chemical analysis is provided in Sections 5 through 10. Chromatography, spectroscopy, x-ray fluorescence, and electrochemical detection along with other relevant methods are included.

This report is a description of sampling methods, analytical techniques, and the entire process of extraction and analysis, its purpose being to enlighten those who are in the decision-making areas as to the depth and variety of possible choices. Through the knowledge gained here, we hope to make this process more efficient, economical, and environmentally profitable.
2.0 GENERAL CONSIDERATIONS

Analytical chemistry before World War II consisted almost entirely of classical wet chemistry and gravimetry. Concentration has a direct, tangible meaning in gravimetry. The sample is either a measured liquid volume or a weighed amount of solid that is dissolved in a known amount of solvent. The analyte species of interest is selectively converted to a precipitate or isolated as a solid with the appropriate choice of reagents and reaction conditions. The precipitate is isolated from the remainder of the sample matrix and weighed. The mass, and hence the concentration of the analyte in the original sample, is determined by calculating the individual mass component of the analyte in the precipitate (reaction stoichiometry). An example of gravimetry is the dissolution of an ore sample and the resulting precipitation of iron.

These techniques have almost completely given way to chromatography, spectroscopy, and other modern instrumental techniques. The shift can be ascribed in part to a greater focus on trace contaminant analysis. The classical gravimetric methods are simply not capable of detecting sub-ppm levels of organic contamination in groundwater.

Modern chemical analysis methods are predominantly instrumental in nature. Over the past fifty years, there has been a pronounced trend toward “electronic” methods and away from classical wet-chemistry methods. The microcomputer revolution dating to the early 1980s has dramatically accelerated this trend. Wet methods employ physical separation schemes and/or chemical reactions with an electronic balance as the only electronic instrumentation. Gravimetry and titrimetry are the two main categories of wet methods; the former has almost totally vanished, while the latter has diminished in importance. Wet operations still exist but are largely restricted to sample treatments, such as extraction, performed in advance of instrumental analysis.

Titrimetric wet methods of analysis persist because they can, at certain times, be more convenient and more accurate than instrumental methods. Generally, such situations involve high concentration situations. Wet methods are rarely advantageous for trace analysis. Examples of common titrimetric methods are Kjeldahl for nitrogen or protein, Karl Fischer for water, and EDTA (ethylenediaminetetraacetic acid) titration for water hardness or total alkalinity determination. Titrimetric methods are commonly used for water quality measurements.

Although instrumental methods are generally faster, have higher throughput, and are often more sensitive and analyte specific, the underlying chemical principles used in instrumental analysis remain the same. Advantages of instrumental methods often remove the focus from the chemical principle, putting the focus on the measurement act itself. This can be seen, for example, in reference made to a gas chromatography/mass spectrometry (GC/MS) analysis, or an atomic absorption run, or a liquid chromatography measurement. These terms describe recent instrumental methods which are based on a chemical principle that does not change.

Whatever method is used, actual measurement falls at the end of a series of previous steps that often have more influence on the quality of the derived information than does the measurement itself. These major steps include:
1. Sample collection
2. Sample transfer
3. Sample shipment (if required) – preservation – storage
4. Sample preparation
5. Measurement

The actions covered by the individual steps are not necessarily mutually exclusive, all or a combination of several of the steps may be required, nor will all steps always follow the order given above. Nevertheless, the measurement itself always lies at the end of a chain of events. Routinely, the analyst does not participate in Steps 1–3 and perhaps not even in Step 4 (if, for example, the sample is extracted in the field). As such, control over the reliability of the final result is often limited by the performance of a number of activities and the persons and equipment involved in each step.

The sample collection step should lead to questions of representativeness. During the collection process, for example, groundwater samples may have their analytes of interest purged or chemically altered by exposure to air, disrupted by the sampling instrument, or degraded by exposure to light. Soils essentially exist as heterogeneous matrices and, therefore, may exhibit large fluctuations in analyte concentrations in subsections of individual samples. Generally, it is best to “homogenize” such samples prior to final analysis. Furthermore, the size of the sampling area is important. Although economic issues are always a concern, sample collection should ideally involve a sufficient area which reliably maps out the extent and quantity of the analyte present.

Sample manipulation almost always includes weighing or volumetric measurement of part or all of the sample. The sample at this time is subjected to a preparative step involving either dilution, preconcentration, or phase transfer. The goal of this manipulation may be to get the concentration of the analyte(s) of interest into the linear dynamic range of the analytical instrument. This step may involve the elimination of interfering species, which could affect the measurement of the analytes. Finally, the actual measurement, although straightforward, can involve extensive prior operations in order to calibrate the instrument.

Contaminants and physical properties of the contaminants which are of interest to the gas industry are listed below. This list should be consulted in conjunction with the analytical techniques described in this work.

Contaminants and Parameters of Interest in the Gas Industry:
- pH and alkalinity
- Conductivity
- Total dissolved solids (TDS)
- Total suspended solids (TSS)
- Total organic carbon (TOC)
- Chemical oxygen demand (COD)
- Biological oxygen demand (BOD)
- Oil and grease
Inorganic Constituents

Metals
Arsenic
Barium
Boron
Cadmium
Calcium
Chromium
Copper
Iron
Lead
Lithium
Magnesium
Mercury
Molybdenum
Nickel

Other Organics
Ammonium
Chloride
Nitrate
Phosphate
Sulfate
Sulfide

Organic Constituents
Aliphatic Hydrocarbons Including Branched and n-alkanes from C4 to C30, e.g., the following:
n-Decane (C10)
n-Dodecane (C12)
n-Tetradecane (C14)
n-Hexadecane (C16)
n-Octadecane (C18)
n-Docosane (C22)
n-Tetracosane (C24)
n-Hexacosane (C26)
n-Octacosane (C28)
n-Triacotane (C30)

Halogenated Hydrocarbons
Chlorobenzene
Dichloroethane
Dichloroethylene
Tetrachloroethylene
Trichloroethylene
1,1,1-Trichloroethane

Phenolics
Phenol
2-Methylphenol
4-Methylphenol
2,4-Dimethylphenol

Polycyclic Aromatic Hydrocarbons
Acenaphthene
Phenanthrene
Anthracene
Pyrene
Benzo(a)pyrene
2-Methylnaphthalene
Fluorene
Naphthalene
**Volatile Aromatic Hydrocarbons**

- Benzene
- Toluene

**Oxygenated Organics**

- Acetone
- Methanol

**Other Organics**

- Anthraquinone
- Disulfonic Acid
- Kerosene
- Amines (diethanolamine, monoethanolamine, methyl-diethanolamine)
- Mercaptans
- Polymers (includ[ing Natural Gums and Carboxymethyl Cellulose [CMC]])
- Radionuclides
- Lead and Polonium

**2.1 Determination of Sampling/Analysis Objectives**

The quality of a chemical analysis is only as good as the quality of the sample upon which the measurement is performed. An extremely precise and accurate measurement on a degraded or nonrepresentative sample is worthless. Therefore, a well-designed sampling plan is essential to meet objectives and regulatory requirements.

DQOs are “statements that provide the critical definitions of confidence required in drawing conclusions from the entire project data.” In other words, DQOs are statements of how the data will ultimately be applied, and therefore, DQOs dictate the degree of sophistication needed in the sampling and in the required analytical instrument. The difference between DQOs and measurement quality objectives (such as precision and accuracy) are that the former are limits for the overall uncertainty of results, while the latter are only limits for the uncertainty of specific measurements.

The goals of an analytical study may be as diverse as source identification, spill delineation, fate and transport, risk assessment, enforcement, remediation, or postremediation confirmation. Optimal selection of sample collection and handling, number of samples taken, and the specific analysis method depend greatly on the intended purpose(s) of the data.

An enormous economic penalty may result when sampling or analytical protocols are inappropriate to the intended purpose of the data and the goal of the study.
Example. GC/MS is the EPA-specified method for quantitation of organic analytes because it combines high sensitivity with high selectivity. Many different analytes can be accurately detected, although at great cost. If there is little or no prior information on the site, GC/MS may be the only method available for complex samples of organic constituents. If a site of previous extensive and diverse industrial activity is being considered for an office complex or a housing development, the prudent developer, even if not legally required, wants to protect himself/herself against the possibility of future litigation by obtaining data for the widest spectrum of contaminants.

However, if the task at hand is to determine how far the contents of a leaking underground storage tank have spread in the surrounding soil, the specificity of GC/MS is not needed. The identity of the contaminant is known, and the cheapest, fastest method that still provides the requisite sensitivity should be selected. The lower cost per analysis allows more samples to be taken and the plume to be better defined. GC/MS may only be necessary for a few samples for regulatory agency requirements.

2.2 Analytical Technique Selection Criteria

It is important to recognize and understand that environmental analysis is an underdetermined problem. There is almost never "too much data." For example, sampling intervals of a hundred feet or more at a hazardous waste site are not uncommon. Short of taking additional samples at intermediate intervals, one cannot guarantee that low concentrations found at two adjacent sampling positions precludes a "hot spot" between them. If there is a significant depth dependence of concentration, the site characterization is even more challenging. The typical approach is to apply computer modeling to construct contours of constant concentration.

In an abstract sense, the "best" analytical technique is the one which gives the lowest detection limits, the highest precision, and freedom from interference. In a practical sense, however, the selection of the most appropriate analytical technique is seldom obvious. Program managers and those responsible for budgeting fully appreciate that state-of-the-art analysis can be prohibitively expensive. Moreover, the most sensitive techniques are likely also to be the most time-consuming and may be incompatible with the project schedule. It may be better to make N times as many measurements for different sampling locations than it is to use a technique that is N times more sensitive; there is little gain in obtaining detection limits of 1 ppb if 1 ppm would suffice. For environmental studies, a technique that gives a precision of 20% may be just as good as one that gives a precision of 5% if the main source of variation is the sampling act itself.

No single technique is always "superior." A choice of technique depends on available human resources, time constraints, budget, and other factors specific to a given problem. The exception, of course, is when a study is subject to regulatory protocols (Environmental Protection Agency, Comprehensive Environmental Response Compensation and Liability Act [CERCLA], Resource Conservation and Recovery Act [RCRA], etc.), and there is no option to those approaches mandated by law. However, there may still be room for negotiation on how many samples will be subjected to detailed analyses. Preliminary screening-type measurements can be
used to justify how many sampling locations are required. The need to make a choice of analytical technique (for screening) arises. It may be necessary to involve a proficient analytical chemist for selection of analytical techniques.

The complete methodology will depend on many other factors in addition to quality parameters. It ranges from the site (field or laboratory) of analysis, economic restraints, personnel (training and availability), sample preparation, sample collection, expected throughput, need for automation, data storage, and the like. Disposal of materials after the analysis must also be considered.

2.2.1 Sample Throughput/Analysis Time

Total analysis time is related to the specific instrumental throughput which dictates how many samples can be run in a given amount of time. For example, because of the unavoidable retention time involved, chromatographic methods usually require more time compared to spectroscopic methods. A trade-off exists between analysis time and resolution which affects the ability to distinguish different eluting components — higher resolution generally results in longer retention time. Spectroscopy usually involves an instantaneous response, although signal averaging and data manipulation often increase the analysis time.

In many conventional methods, the actual analysis time (i.e., measurement time) is small compared to the sample preparation time which begins with transfer and shipping to the analytical laboratory for further operations such as extraction, concentration, and chemical transformations (oxidation, reduction, complexation, and derivatization).

In certain situations, field screening is desirable to obtain numbers for concentrations even if they are approximate. Methods designed specifically for field conditions are required.

Laboratory and personnel scheduling should be kept in mind. Often, the first samples submitted for testing will be the first results returned. If you are submitting a large quantity of samples or if additional sampling will occur later, you may wish to organize your submission so that specific samples are “first in — first returned.” These first results may provide insight useful to later sampling or on how best to analyze other samples.

2.2.2 Analysis Cost

Capital costs associated with analytical equipment can range from one to four orders of magnitude. Simple wet-chemical analysis methods, available in a test kit format are available for approximately $10/sample, whereas very sophisticated instrumentation can easily exceed $200,000/unit. Obviously, one must consider the number of samples over which the capital acquisition cost will be amortized.

Generally speaking, the more expensive analytical instruments require a higher level of training for operation. The necessity for highly trained operators will increase overall costs. If contaminants of interest have been identified, a test kit and other field-screening approaches can
work extremely well. However, they are not nearly as suitable for sensitive detection of specific analytes. When determining cost, the purpose, choice of methods and, finally, the operational level of training necessary to carry out those methods must be taken into consideration when determining cost.

Regulatory compliance is also a factor. The analytical methods necessary to demonstrate regulatory compliance tend to be more traditional in nature. They are not always the most sensitive, selective, technologically simple, or even economical. These factors are often overridden by the well-behaved character of the traditional method. A good example is GC/MS analysis of volatile organic compounds (VOCs). A full GC-MS determination is very expensive and often time-consuming. An analytical testing lab is the usual venue for testing.

2.2.3 Degree of Automation

Many operations can be automated for repetitive tasks. For example, GC and high-performance liquid chromatographs (HPLC) come with autosampler options. A carousel loaded with dozens of samples allows for analysis on a larger scale. Robotics has an obvious role in increasing the degree of automation. The determining factor in automation is the number of samples being run. The number must justify the time and expense of automation.

Often sample preparation involves several unit operations which can be performed with the aid of automation. The technique of flow injection (injection of a discrete volume of the sample into a moving carrier stream) is generally used. Chemical reactions occur in the stream and convert the analyte to a working form (colored complex, hydride, etc.) required by the technique. It is also possible to perform unit operations such as standard additions, dilutions, ion exchanges and sorbent preconcentrations on the sample aliquot in a flow injection mode. Chemical reactions such as derivitization can also be automated.

2.2.4 Required Operator Skills

Required operator skills range from minimal, as needed to use the simple water analysis test kits, to a highly technological level such as that required in the operation of spectrometers and chromatographs. The Hach-type water analysis test kit demands only a few sequential operations, after which, a color and intensity comparison of the sample is made to a set of standards. These test kits are designed so that all reagents are preweighed and premeasured.

The very sophisticated GC and GC/MS instruments, on the other hand, require well-trained operators. Manufacturers often make common practice of offering specialized operator courses aimed at proper use and maintenance of their equipment. Data analysis or methods development could require the services of an experienced analytical chemist.

A skilled operator is an asset to any testing program. Experienced personnel may identify potential problems before they occur and can be invaluable to an inexperienced or overwrought program manager in assisting with data reduction and interpretation.
2.2.5 Compatibility for Field Use

The question of field compatibility for instrumental analysis has become a growing concern among the environmental analysis community. Ideally, if all relevant analytical instrumentation could be made field-compatible, while maintaining the degree of accuracy and precision currently available in stationary laboratories, errors caused by problems with sample shipment, preservation, and storage (Section 3.5) could be eliminated. This would effectively translate into economical use of time and money and reliability of test samples. Currently, however, field compatibility is still being perfected. At this point, current state-of-the-art field-compatibility among analytical instrumentation and the degree of reliability these instruments afford in their analysis must be considered. With the advancement of current technologies, field-compatible techniques will be the goal toward efficient and economic methods. EPA program administrators state:4

"Field analytical methods are typically not as rigorous as chemical analyses conducted in a “fixed” laboratory – a laboratory in a permanent location. Field methods are often used for screening sites to determine if contamination is present and to obtain a general idea of the extent of contamination. Further, field analytical methods are most useful when the contaminants of concern have already been identified, so that the appropriate methods, dilutions, calibration, ranges, etc., can be employed. In addition, field analytical methods are usually designed to identify only a limited number of analytes. Recently, however, more sophisticated and more rugged instrumentation have allowed for more rigorous analyses in the field; consequently, field analytical chemistry does not have to be limited to screening. Even so, it is generally believed that field analyses provide less precision and accuracy than analyses conducted in fixed laboratories. It should be noted, however, that despite this perception, a focused gas chromatographic analysis is likely to be better than a heavily quality-controlled GC/MS screen. The data quality is not compromised, since field analyses are usually conducted in conjunction with confirmatory analyses, such as GC/MS or ICP/MS analyses using EPA Contract Laboratory Program (CLP) protocols. Consequently, field analyses are often used to identify samples for more rigorous, CLP-type analyses."

A few of the most common techniques engineered for field service include HPLC, GC/MS, and x-ray fluorescence (XRF). These techniques are described in subsequent sections. The key to readapting these methods to field scenarios involves minimization of size, decreased power requirements, and higher degrees of ruggedness. The consensus in regard to their field use is that they provide certain niche applications that do not yet encompass the full versatility available to these techniques in a stationary laboratory. Obviously, the use of test kits and immunoassay methods (Section 10) are readily applicable to a field setting.
3.0 SAMPLING

The objective of a hydrologeologic site investigation is to accurately assess soil and/or groundwater contamination in order to design adequate and cost-effective remediation methods. Proper planning and sampling are the first steps in the assessment. The sampling process actually begins with communication between the gas industry and lab personnel. The importance of communication throughout the process must be stressed as lab personnel should be afforded quick and easy access to any information regarding requirements and goals of the program, sample shipment schedules, and any anomalies with the samples. Lab personnel may be expected to review and refine the requirements and/or develop a detailed quality assurance project plan (QAPP) for large projects. Communication with lab personnel also offers knowledgeable advice concerning sample containers, specific preservation techniques, and equipment decontamination.

Sampling represents the first step in the analysis process for unknown chemical species. Sampling is an integral part of the whole analysis process and definitely should not be overlooked as a minor step in the acquisition of testing material. The act of sampling can take on several different forms depending on whether the sample is gaseous, liquid, or solid. Measurement/analysis occurs after a series of sampling activities. It is crucial, therefore, that gas industry personnel have an understanding of the effects that these actions have on the final measured value. Regardless of the phase of the matter, several key issues apply to the manner in which sampling occurs. These key issues are described below.

3.1 Objectives of Sampling

"Objectives of environmental sampling are broadly divided into exploratory (surveillance) or monitoring (assessment) goals." Exploratory sampling is designed to provide preliminary information about the site or material being analyzed. Monitoring, on the other hand, usually is intended to provide information on the variation of specific analyte concentrations over a particular period of time or within a specific geographic area; monitoring is used for regulatory (enforcement) and nonregulatory purposes.

A distinction is drawn between surveillance and screening, which is defined as "preliminary sampling... to help delineate the extent of contamination and the variations in contaminant levels within the affected area." During the screening process, it is important that both the sampling and subsequent analyses be performed under the same sampling, analytical, and QA/QC (quality assurance/quality control) protocols as those developed for the main body of test samples. If this is not performed properly, the sampling may produce invalid data and false conclusions. This is a conservative viewpoint.

3.2 Trained Personnel

According to an EPA estimate, 80 percent of error associated with accurate sample characterization can be attributed to actual sampling activities, 15 percent to subsampling (transfer, shipping and handling), and 5 percent to laboratory activities during analysis. Traditionally, greater attention and financing are placed on QA/QC. In view of the importance of
correct sampling procedures, it is obvious that more emphasis needs to be placed on training field personnel to ensure sample integrity from collection to shipment.

Care should be taken that the sampling team be familiar with EPA protocol and the policies of the lab with which they are dealing. They should have the required health and safety training and should also be experienced with the field analysis methods being used (e.g., some wet-chemistry experience is necessary to obtain reliable results with immunoassays).

Samples can be split and sent to separate laboratories for the purpose of producing comparative results. Submission of spiked samples, containing one or more compounds that are purposely added at known concentrations, or blank samples can also be used to periodically check a laboratory’s testing procedures. See Section 4.4 for further discussion.

It is advantageous to use the same team or key personnel when conducting sampling activities in multiple locations in order to ensure consistency of method and protocol adherence (Section 3.4), which in turn reduces the possibility of variations related to sample handling.

3.3 Sample Collection

It is critical that a representative set of samples be obtained. There is always a budget-imposed upper limit to the number of samples allowed. The larger the site is, the greater the likelihood that a limited number of samples will miss localized hot spots arising from point sources. A well-devised sampling plan will take into account past activities at the site in an effort to make the most appropriate choice of sampling points. “Statistical Methods for Environmental Scientists” is an excellent desk reference for nonstatisticians attempting to answer questions concerning sampling adequacy and statistical significance. Past activities will indicate the possible presence of particular waste types. To determine that samples are representative of the waste being generated, the sample coordinator must be thoroughly familiar with the processes at the sampling site.

Field-screening methods are attractive because they can provide cost-effective real-time guidance for the selection of sampling locations. A less accurate method involves taking more samples and combining a number of them, thus reducing the number of actual analyses performed. This decreases the odds that a hot spot is missed, but pooling such samples unfortunately increases the minimum detection limit while diluting the effect of a hot spot. Combining samples can be economically efficient but may not always be acceptable in terms of analytical results.

The sampling team should familiarize themselves with the processes at the site to determine that samples are representative of the waste being generated. Information regarding sample type, location, equipment type, and method of collection should be included with the samples. Weather-related environmental conditions such as atmospheric pressure and odors are also important and should be recorded.
An excellent overview of groundwater sampling is provided in Chapter 2 of the EPA document entitled “Handbook – Ground Water, Volume II: Methodology.” The chapter contains a discussion of well drilling and development, sampling point selection, sampling protocol, sample handling, and other groundwater-related issues. Because of its pertinence to this report, the complete chapter has been included as Appendix A.

The Wisconsin Department of Natural Resources publication, “Groundwater Sampling Procedures Guidelines,” is another thorough source of information. The American Society of Agronomy is a source for information specific to soil sampling and soil analytical procedures. Selected monitoring well and soil-sampling methods, approved by the American Society for Testing and Materials (ASTM), are included in Table 3-1 below.

<table>
<thead>
<tr>
<th>Method Number</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>D 5092-90</td>
<td>Design and Installation of Ground Water Monitoring Wells in Aquifers</td>
</tr>
<tr>
<td>D 653</td>
<td>Terminology Relating to Soil, Rock, and Contained Fluids</td>
</tr>
<tr>
<td>D 1452</td>
<td>Practice for Soil Investigation and Sampling by Auger Borings</td>
</tr>
<tr>
<td>D 1586</td>
<td>Method for Penetration Test and Split-Barrel Sampling of Soils</td>
</tr>
<tr>
<td>D 1587</td>
<td>Practice for Thin-Walled Tube Sampling of Soils</td>
</tr>
<tr>
<td>D 2113</td>
<td>Practice for Diamond Core Drilling for Site Investigation</td>
</tr>
<tr>
<td>D 2487</td>
<td>Test Method for Classification of Soils for Engineering Purposes</td>
</tr>
<tr>
<td>D 3550</td>
<td>Practice for Ring Lined Barrel Sampling of Soils</td>
</tr>
<tr>
<td>D 4220</td>
<td>Practice for Preserving and Transporting Soil Samples</td>
</tr>
</tbody>
</table>

3.4 Sample Transfer

In the conventional (ex situ) approach, the sample must be transferred from the sampling device to the container prior to its shipment to the laboratory. This is an especially crucial step for VOCs. Too much agitation of a groundwater sample or excess manipulation can easily result in the volatiles being permanently lost into the atmosphere. The concentrations reported at the end of the sampling/analysis chain will then suffer from a negative bias (inaccurately low results). Experiments have demonstrated that concentrations may be underreported by a factor of five or more owing to loss of volatiles. Pooling or homogenizing samples runs this risk. In situ analysis techniques have the potential of eliminating the sample transfer step entirely, but unfortunately these are still in an early stage of development.
3.5 Sample Shipment, Preservation, and Storage

There is commonly a time lag, possibly as long as several weeks, between sample collection and analysis. During this interval, the analyte concentrations can change owing to various chemical, physical, and biological processes. For instance, volatiles are subject to release from solution or into the headspace of a solid sample. If shipping containers are not airtight, the volatiles can be lost during shipment, storage, or when the container is opened in the laboratory. Pressure and temperature fluctuations (e.g., in commercial airplane cargo bays, these vary widely during the course of a flight) also increase the possibility of changes in the sample. Organics are subject to chemical reaction with oxygen or other species present in the sample. Certain aromatics can undergo photochemical degradation. Microbial degradation is also a concern. Note that all these factors act in the direction to introduce negative bias. With inorganic samples, a major concern is oxidation/reduction processes affecting metals, and so control of sample pH can be an issue. Handling issues specific to groundwater samples are detailed in Appendix A, including a sample chain-of-custody record.

3.6 Sample Preparation

Most methods require some type of preanalysis manipulation of the sample. Examples include extraction, preconcentration, or filtration. There are numerous preparation schemes for practically any analytical method; therefore, a thorough discussion cannot be given in this report. As a general guide, however, the reader should understand the nature of the analysis and the kind of general preparative steps which would be needed for that analysis. For example, a common concern in sample preparation involves the extraction efficiency of organic waste products in soil samples. Soil samples are generally rich in organic material; therefore, an extraction scheme which uses an appropriate solvent is required to extract the species of interest. Ideally, this occurs while simultaneously minimizing the solvation of undesirable organics. It should be noted that volatiles are still likely to be lost at this stage. Chemical changes that occur during sample preparation are also potential sources of error in this step.

Purging. Purging (sparging) efficiency is never 100%, meaning that purging never transfers 100% of the analyte to the trap. In general, it is more important that the purging be reproducible than efficient. If the same amount of analyte is transferred in repeated purging with the same experimental protocol, it is considered reproducible. It is generally acceptable if only 10% of the analyte is transferred to the trap during a 10-minute purge. Purging efficiency can be affected by the temperature of the purge vessel. Higher temperature increases the volatility of gaseous species, increasing flow rates. Greater sparge gas flow rates generally result in increased mass transfer of the analyte to the analyte trap. The presence of other analytes can affect the sparging.

Laboratory standards do not always serve as reliable means for analyte quantification or calibration. For example, efficiency of sparging benzene from a water solution will not mirror the efficiency of sparging benzene from a solution with a high concentration of dissolved organic matter (or a different solvent). In a solvent other than water, if benzene is highly soluble, that solvent preferentially retains the benzene in solution. In other words, the sample matrix influences purging efficiency.
Ideally, standard solutions would be prepared from a matrix containing everything except the analyte of interest. However, this is often impossible owing to the singularity of environmental samples and their high degree of heterogeneity. For example, the addition of standard solution to soil matrices often requires lengthy periods of time (days to months) to reach a fully equilibrated state.

In nearly all commercial instances today, monitoring well sampling is completed by field personnel of contract laboratories or consulting firms or, in fewer cases, qualified in-house personnel. Regardless of how project responsibilities and tasks are organized, a proper groundwater sampling methodology, well understood by all involved, is crucial to accurate contaminant characterization and site assessment. Driscoll lists the major pitfalls that can affect sample representiveness as the following:

1. The sample was drawn from stagnant well water. Aquifer transmissivity should be calculated, and in most cases, a sample is drawn only after three to ten well-bore volumes have been removed. Proper procedures will ensure that at least 95 percent of the water being sampled comes from the target aquifer. Sampling of water should not occur if it has been in the well casing (interacted with the atmosphere and well casing) for more than about 2 hours (Appendix A).

2. Samples were not drawn at appropriate frequency intervals. The faster the rate of contaminant movement is (based on hydraulic conductivity), the more frequent sampling required.

3. Poor monitoring well development that has lead to contamination of samples by entrained sediment. Contaminants that are adhered to sediment may be released into the water sample.

4. Sample representativeness was affected by inconsistencies in the hydraulic character of the geologic formation. Contaminant levels may become diluted or concentrated because of changes in hydraulic conductivity and permeability.

5. Sample representativeness was affected by delayed sampling during well pumping. Too much time has passed during pumping so that sample represents groundwater far from the well site.

6. Precipitation of metallic ions was caused by release of carbon dioxide and subsequent rise in pH during pumping.

7. Sample was oxidized during recovery either in the pump or by turbulent flow into a tight formation well. Stumm and Morgan listed changes that can occur in reduced groundwater (a common state), including oxidation of:

- Organics
- Sulfide to sulfate
• Ferrous iron and precipitation of ferric hydroxide
• Ammonium ion to nitrate
• Manganese and precipitation of manganese dioxide or similar hydrous oxide

8. Sample was contaminated by residues in the pump or other equipment. Equipment must be either dedicated to a single well or properly cleaned with each use.

9. Sample was affected by improper preservation. Chemical changes can occur during storage (see Section 3.5). The two most common precautions are refrigeration and protection from light.

10. Sample was adversely affected by lag time between sampling and analysis because of shipping or proper laboratory scheduling (see Sections 2.2.1, 3.4, 3.5).

11. Samples were not analyzed properly. The smallest error in analytical work can produce erroneous results, especially when dealing with concentrations of parts per billion or parts per trillion (see Section 3.5).
4.0 ANALYTICAL CONCEPTS AND TERMINOLOGY

Apart from the concerns of sampling, one must understand the suitability of a particular analytical method in regard to its intended use. Method validation is a process by which the performance of an analytical method is characterized. The validation process must be performed under conditions that most resemble the procedure which would be undertaken for the actual analyte studies. Ideally, this includes using samples with similar matrices, using the same sample preparation steps, and using the same experimental parameters that one would expect to use for the actual sample. Method validation protocols should always be documented for future reference. The factors which compromise the method validation process include those concepts related to the calibration curve (Section 4.2), along with the concepts of limit of quantification, instrumental ruggedness, and stability. Since method validation is inherently an instrumental concern, the basic ideas underlying modern instrumental detection should be understood.

4.1 Nature of Instrumental Methods

Even though the concepts of concentration and amount (as in a detection limit) are pervasive in chemical analysis, one should remember that what is really measured in most forms of modern analytical chemistry is simply a detector response. One must establish the analyte concentration by comparing the instrumental response of the sample to that of standards. A direct relationship between detector response and analyte concentration is assumed, but there are many factors that can affect and distort the response factors. Electrochemistry can come closest to providing a direct relationship between the analyte and its concentration. For example, pH is related to the hydrogen ion concentration, and the potential of an ion-selective electrode is similarly related to ion concentrations. A well-defined mathematical relationship exists between pH and hydrogen ion concentration as described by the Nernst equation which relates the voltage of a cell to the activities of reactants and products.

However, in chromatography and most forms of spectroscopy, the process is far more involved. We are led to the concept of calibration curves and the related analytical figures of merit: sensitivity, detection limit, precision, accuracy, and linear dynamic range. Techniques vary with relevance to each concept. An explanation of each follows.

4.2 Calibration Curves

The strength of the detector signal is a function of the concentrations of all analytes present in the sample to which the detector responds. A well-defined and reproducible relationship between detector signal and concentration must be established by some standardization/calibration procedure before a means for finding concentrations in unknown samples is available. In the ideal case, the detector signal, denoted I, is directly proportional to the concentration C of a single analyte, independent of other chemical species in the sample. If the signal for the unknown is three times that of the standard, then the analyte concentration in the sample is three times that in the standard. Real life is obviously not this simple. The main purpose of this chapter is to identify as many of the complications as possible.
Calibration is the systematic determination of the relationship of the response of the instrument system to the concentration of the analyte of interest. The usual representation of the results of that systematic determination is a calibration curve (also known as an analytical curve), which can graphically be represented as a plot of detector response versus concentration. For the ideal case of the last paragraph, the calibration curve is a straight line passing through the origin (Figure 4-1). This is the expected result since no signal should be observed in the absence of analyte. A single measurement at a given analyte concentration verifies the calibration.

Distortions are inevitable at both the low and high ends of the concentration range. The flattening of the analytical curve at low concentration is likely a consequence of background signals. These signals can be caused by detector dark current (in a PMT), or by overlapping signals from other species (more likely in real samples). As the concentration of an analyte is progressively reduced in the standardization process, its contribution to the measured signal is overwhelmed by those of the inevitable background signals.

At high analyte concentrations, flattening of the analytical curve is also common owing to, among other factors, detector saturation. The distortions in the high concentration range are varied. It is even possible for the signal to decrease with increasing sample concentration past a certain point, (i.e., monitored light emission after excitation). At high concentrations, unexcited analytes reabsorb some of the light previously emitted, resulting in an overall decrease in the light impinging upon the detector. Logarithms of both concentration and intensity can be conveniently represented for calibration curves which extend beyond one or two orders of magnitude concentration range.

Figure 4-1. Points of signal intensity as a function of analyte concentration. Note the linear relationship of the response.
The concentration range over which the analytical signal changes linearly with concentration is known as the linear dynamic range (LDR). The LDR is a subset of the analytical concentration range. It is often expressed in terms of orders of magnitude. For example, a linear relationship for concentrations between $10^{-9}$ and $10^{-5}$ M (molar) means an LDR of $(9 - 5) = 4$ orders of magnitude. It is not mandatory to work in the LDR to obtain reliable results, but within this range, techniques are regarded as most reliable; therefore, a wide dynamic range is clearly desirable. If the analyte concentration in the sample is so high that the signal is above the LDR, one can either dilute the sample or change the detection sensitivity. A concern with concentrated samples is that the "out-of-bound" condition is not detected, resulting in the possibility of spurious values. Preconcentration of samples to a higher range is an optional method when the concentration to be measured falls below the dynamic range. Alternate techniques can also be employed.

The method of standard additions involves adding small amounts of a standard solution or analyte to a sample. Subsequently, one measures the absorbance or signal resulting from the addition of the analyte. These steps circumvent the identification of interfering components and maintain the sample matrix with only minor dilution of the sample. In determining the original concentration of the analyte of interest in the sample matrix, a plot of added analyte against signal intensity is constructed. Figure 4-2 demonstrates this procedure. Since the first point plotted is 0 (no analyte added) and standard additions linearly increase the response of the analyte signal, we can extrapolate the calibration curve to the x-axis intercept. The region bounded by the x-axis intercept and the point representing the free sample is the measure of the original analyte concentration.

![Figure 4-2](image)

Figure 4-2. The extrapolation method used to determine the starting concentration of a mixture.\(^5\)
Full analytical calibration curves are taken at various stages of analysis. Instruments should be calibrated at the beginning of a project before any samples are analyzed, after each major disruption in analytical procedures, and whenever action limits are exceeded for certain samples. Most standard methods state the calibration frequency, however, the initial calibration is a time consuming, often tedious, and expensive process. A wide linear dynamic range can mean longer intervals between initial calibrations.

The validity of the original calibration curve must be confirmed throughout the analyses of samples in a process known as continuing calibration. Continuing calibration in the best of circumstances requires running at least one known sample to verify that the instrument response is consistent with the initial calibration and the established accuracy and precision of the methodology. Precision of methodology is discussed in Section 4.6.

4.3 Detection Limit

The signal from a detection system invariably contains a detector noise component, as well as other background signals, along with the signal of interest. When an analyte is present at low concentration, the ability to distinguish the true signal from the noise and/or background is reduced, and the limit of detection is reached. The smallest amount (concentration or mass) that can be detected with a stated statistical confidence is referred to as a detection limit. Detection limits are based on the variability of either the blank response (see Section 4.4) of a method or the variability of the response for a low-level standard.

One common definition relates the detection limit (DL) to $\sigma_b$, the standard deviation of the blank measurement by

$$DL \text{ (concentration)} = 3 \sigma_b / S$$

[Eq. 4-1]

where $S$ is the sensitivity (Section 4.5). This definition is based on the assumption that error (noise) in the background measurement is normally distributed. In this definition, there is a 99.85% probability that a signal that exceeds the background (blank) signal by more than 3 times the standard deviation of the background is a real signal. In practice, the noise signals are not distributed in Gaussian fashion (Gaussian meaning the theoretical bell-shaped distribution of measurements; all error is random, the center of the curve is mean, and the width is characterized by the standard deviation) and can, in fact, be significantly asymmetric. In such a situation, the confidence limit from the above is about 90%. Note that it is the standard deviation (the "variability or fluctuation") of noise rather than the magnitude that enters into the detection limit determination. A very high, but extremely stable noise level may well be preferable to a lower, but more variable noise level. Since the noise level fluctuates randomly with time, the longer the measurement time is, the greater the likelihood that random noise will be averaged out to form a lower "variability" in the baseline measurement.

The detection limit can be expressed in terms of either mass or concentration. Whether absolute mass or the concentration representation is more relevant depends on the amount of sample that is available. The concentration limit is more relevant when the amount of sample is
not limited (which is usually the case in environmental problems). Sample limited situations are more likely to arise in forensic applications or in the biological realm. The mass detection limit is perhaps more meaningful when there is an upper limit on how much sample can be presented to the instrument. The following example demonstrates this concept.

Example. Suppose the detection limit in a GC application is stated to be 1 ng \( \left( 10^{-9} \text{ g} \right) \), which is an impressively small number. However, when one realizes the typical sample injection is 1 \( \mu \text{L} \), the concentration detection limit is seen to be 1 ng/\( \mu \text{L} \) = 1 mg/L = 1 ppm, which is still a low concentration, but perhaps a few orders of magnitude greater than the suspected concentration of the analyte of interest. In such cases, it is necessary to preconcentrate the sample prior to the actual injection and chromatographic separation.

Not all of the analyte in the sample aliquot presented to the instrument may reach the detector. This affects the volume/mass/amount sample needed to perform the analysis. Graphite furnace atomic absorption (GFAA, Section 6.6), offers greater detection ability (lower limit of detection) than does flame atomic absorption (FAA, Section 6.6) because the sample remains in the light path for a few seconds as opposed to a fraction of a second with FAA.9

Nebulization occurs when particles are formed through the direction of a spray (fine mist) against a glass bead. The spray (droplets of analyte solution), which is forced against the bead at a high speed, is broken into smaller particles and passed through several baffles for mixing and filtering of larger drops. About 5% of the initial sample, in the form of a very fine mist, actually reaches the flame.

The limit of detection is the lowest concentration or mass of an analyte that can be statistically measured. The limit of quantification is defined as the amount of analyte which results in reproducible measurements of peak areas. The goal is usually to identify and quantitate the amount of analyte present in a given sample; therefore, a rational means of standardizing this process is necessary. Peak areas are utilized in many analytical techniques as a means of analyte quantification. However, under dilute conditions and very near to the limit of detection, integrated measurement of the peak areas cannot be relied upon as statistically meaningful. Baseline noise and actual peak area cannot be differentiated under dilute conditions at the limit of detection. The general consensus is that peak height measurements must be on the order of 10–20 standard deviations above baseline noise before actual peak areas become statistically reliable for quantification purposes.

A thorough analytical scheme which encompasses the concepts described above requires blanks and QC samples relevant to determining the extent of background and undesirable analyte interactions. The use of blanks and QC samples is described in detail below.

### 4.4 Blanks and Quality Control Samples

Blank solutions contain all chemical species that will be present in the standards and samples to be measured (at equal concentration levels) except for the analyte species. Such a
solution should not display any absorption; thus $I_0$ represents the maximum intensity that can
strike the detector. When the blank is replaced with analyte, a less intense light beam is detected.
See Appendix A, Table 2-5, for a listing of field standards and sample spiking solutions. Several
types of blanks are described below.

4.4.1 Method Blank

The concept of measurement for a blank or background signal is integral to the notion of a
detection limit. Method blanks are defined as matrices (samples) that have negligible or
unmeasurable amounts of the analyte of interest, but are otherwise identical to the samples.
Background measurements are made on the blanks in a fashion as similar as possible to the
method used for the samples. Solvent blanks (mixture of solvents used to dilute samples),
reagent blanks (solvent blank + reagents), and sample blanks (solvent blank + sample) are often
used to correct for solvent effects, solvent and reagent, solvent and matrix effects, and
contamination. Reagents are used in many spectroscopic and nonspectroscopic techniques at the
sample preparation stage for analysis. Reagent blanks are prepared from all of the reagents but
without the analyte. The response of the analytical method to impurities or other effects in the
reagents or other components is measured. If the sample matrix is known, a matched-matrix
blank can be used. It is prepared by mixing all constituents other than the analyte. An internal
blank, which comes closest to the matrix, can also be made by selective destruction of the
analyte.

4.4.2 Quality Control Blanks

Other kinds of blanks are part of the quality control process and can be used to assess
contamination from sources external to the sample. Such sources include contamination from the
analyte container, the storage or transport of the samples, or the field-sampling equipment. The
types of blanks which reflect these concerns are bottle blanks, transport (trip) blanks, and field
equipment blanks, respectively. Bottle blanks, as their name simply implies, are used to
determine the extent to which contamination arises from the storage media. Generally, this is
prepared for each lot of samples taken. Inexpensive precleaned sampling containers are often
used by reputable laboratories, in which case the need for this particular blank may be less
necessary. Transport blanks are clean sample containers filled with highly purified (deionized)
water. These are shipped out with the contingent of sample containers to be used in the field. If a
transport blank demonstrates a large degree of contamination, there is a problem with the method
in which the samples are stored or transported. Transport blanks are particularly important in
regard to volatile organics which can diffuse across sample containers during the course of
transportation or storage. Finally, field equipment blanks are useful for detecting contamination
due to sample perturbation caused by the field equipment. Field equipment blanks should be
taken for each medium sampled.

4.4.3 Matrix Spikes

Similar in nature to the blanks described above, matrix spikes are used to assure a degree
of quality assurance in the analysis process. Specifically, matrix spikes are used to determine the
nature of matrix effects along with the precision of the analytical testing. Matrix spikes consist of known amounts of analyte(s) added to a sample, usually before extraction and sample preparation. As such, they can be used to determine the degree to which an analyte is bound to its matrix. Matrix spikes are performed in conjunction with replicate, unspiked samples such that the response of a particular analyte can be assessed during the analytical process. By spiking samples prior to digestion, extraction, or dilution, one can determine the effects of each of these steps in the binding of the analyte to the given matrix. This is particularly applicable to metal analysis in which the metal analyte can be readily added at certain steps along the preparatory process.

There are several key issues regarding the manner in which spiked matrices are utilized. Typically, the widest possible range of analytes should be included in the matrix samples. For the analysis of semivolatiles, a recommended amount of three neutral compounds, two organic acids compounds, and two organic base compounds is given. Normal concentrations for the spiking material are approximately 5 times the value naturally expected in the sample. This value is sufficient to eliminate the masking of spectral interferences at the assumed concentration of the chosen analyte. The spiking concentration also assumes a reduction in random error associated with the spike analysis. Spike samples and one duplicate spike sample are generally performed for every set of 20 or fewer samples. Batches greater than 20 samples can be broken down into sets of 20 and subsequently analyzed. In this fashion, spike analysis can be used to test the precision and bias of the sequential batches.

4.4.4 · Surrogate Spikes

Surrogate spikes consist of compounds that closely resemble the molecular structure of the analyte of interest and are used only when the surrogate can be identified. The spiking compounds for some organic constituents can consist of deuterated versions of the actual analytes or, for instance, can consist of brominated versions of common polychlorinated contaminate. Surrogate spikes are added to an analytical sample and are primarily used to determine the extent of the recovery of organic compounds. Their similarity to the compound of interest allows for priority checks which evaluate analytical recovery. Because there is a known amount of added surrogate, the recovery for that surrogate is also known and can be compared to the recovery of the analyte of interest. In the analysis of semivolatiles, five surrogate compounds are generally recommended for spiking in a manner similar to that described for matrix spikes. VOCs are recommended to be spiked with at least three neutral compounds. Surrogate spiking is performed during the analysis of PCB's and pesticides. Although an accepted methodology, spike recoveries do not always mean analyte recoveries. Differences may relate to sample heterogeneity and preparation of QC samples.

4.4.5 Check Standards and Spiked Method Blanks

Check standards are known amounts of analyte that are analyzed at the same time as the samples. Their purpose is to serve as indicators of bias in the sample preparation or in the existing calibration. The use of several check standards over a given time provides an indication of the instrumental precision.
Spiked method blanks consist of surrogate spikes which are added to check standards. Their use is generally limited to organic methods when no suitable reference material (see below) is available. Their purpose is to serve as a means of QC in the analytical process. The degree to which the samples are spiked is dictated by the EPA's guidelines for CLPs. Spiked method blanks are used the first time a method is performed or after any modification of the analytical process.

### 4.4.6 Reference Materials

Reference materials consist of check standards with well-characterized chemical compositions and may include aqueous solutions and soils. These materials can be acquired from certifiable sources to allow for comparison of accuracy and precision for the measurement of a particular analyte. Testing the merit of analytical methods often takes place over long periods of time. Since reference materials for testing are well characterized, proper storage environment is crucial. Any contamination or long-term exposure to the atmosphere will affect the chemical content and concentration of the reference material components; therefore, these materials should be carefully checked upon receipt and after storage. Reference materials can readily be purchased from the following federal laboratories:

- **US Environmental Protection Agency**
  - Environmental Monitoring Systems Laboratory
  - QA Research Division
  - 26 W. Martin Luther King Way
  - Cincinnati, Ohio 45268
  - (513) 569-7325

- **1990 Standard Reference Material Catalog**
  - National Institute of Standards and Technology
  - Office of Standard Reference Materials
  - Building 202, Room 204
  - Gaithersburg, Maryland 20899
  - (301) 975-6776

### 4.5 Sensitivity

The greater the change in the signal $I$ per unit change in the concentration $C$, the more sensitive is the measurement. Sensitivity is mathematically defined as

$$S_j = \left( \frac{\partial I}{\partial C_j} \right)$$

[Eq. 4-2]

where $j$ indicates the jth analyte and $i$ indicates the other species present. A more elementary working definition is $S = (dI/dC)$, where other components present in the sample are assumed to be noninterfering with the signal being monitored. Sensitivity should not be confused with the
detection limit; the two are related but not synonymous. S is determined from a calibration curve. The slope of a tangent line on the calibration graph at a given concentration (C) is the numerical value of the sensitivity at that concentration and wavelength. A steeply rising curve means high sensitivity, and a flatter curve means lower sensitivity. If sensitivity is constant over the concentration range, then one obtains a straight line graph with slope of unity for the log I vs. log C plot. Note that sensitivity cannot be determined by a direct examination of the calibration curve in the log-log format.

The essential virtue of high sensitivity is that a smaller change in concentration is required to give a measurable change in detector signal. All other factors being equal, a high sensitivity method is preferred over low sensitivity for trace constituents. However, low sensitivity may well be compensated if the uncertainty of the value from the detector signal is correspondingly small. It is often possible to vary the sensitivity by manipulating the gain of the instrument. Changing the gain of amplifier stages via voltage supplied, for example, may (or may not) improve the signal-to-noise ratio (S/N) and detection limit. Varying the sensitivity is the preferred method in cases where low concentrations of analyte must be detected.

It might seem that optimization of the signal is the key to optimization of an analytical determination. However, this is not so, nor is it satisfactory to minimize the noise. Rather, optimum performance of an instrument requires maximization of the signal-to-noise ratio, which requires simultaneous adjustment of many different instrumental parameters. Graphical approaches are usually required to find the best set. In certain situations, it is possible to derive analytical expressions for S/N.

### 4.6 Precision and Accuracy

Precision refers to the repeatability of a measurement. When a measurement is repeated under ostensibly identical conditions, there exists a variability in the results which often conforms to a Gaussian distribution. The smaller the variation in the value obtained in different trials, the higher is the precision. Precision is commonly confused with accuracy. The two concepts, albeit related, are not the same (Figure 4-3). An analysis can be precise but inaccurate, for example, when an instrument is improperly calibrated in a consistent way such that all the values are consistently higher or lower than the proper value.

Many factors contribute to precision. Instrument specific S/N, unit operations carried out during the sample preparation, and the sampling act itself are most important. It has already been pointed out that the latter two factors can easily dominate the actual measurement in terms of degrading precision. Presumably the greater the number of steps there is in an analysis, the lower the precision. Probably most notorious for lack of precision is VOC analysis.

Precision is as important a parameter when not working in the region near the detection limit as it is when working near it. Very dilute samples can often be preconcentrated to avoid working at the detection limit. Precision generally holds merit with concentrations over the limit of quantification (Section 4.3) and remains constant over the analytical range where the concentrations exceed the detection limit by at least one order of magnitude. Precision is
Figure 4-3. Relationship between accuracy and precision. Target center is “true value.”

Accuracy is a measure of how well the value for a determination agrees with the “true” value (which implies that the true value is known). For environmental situations, the term accuracy is less meaningful in its literal sense. However, it is still essential for verifying the methodology for an analysis using known standard reference materials (Section 4.6.6). Significant deviations for standards may indicate a calibration error, gross differences between the real matrix and the standards, or interferences. Accuracy is always equal to or lower than the precision of the analytical procedure. Figure 4-3 illustrates the four general examples encountered in relating precision and accuracy.

Normal random fluctuations in instrument operations may introduce bias into the final analysis. Whether because of the technology of the instrument, the method, or the operator’s technique, bias can have an effect, however small, on accuracy and precision.
4.7 Selectivity and Specificity

Selectivity and specificity are often used interchangeably, although subtle differences exist in their meanings. Specificity is properly used in reference to an analytical method which produces a response from a single analyte. Selectivity, however, is used in reference to a method which provides responses from a variety of analytes which may or may not be distinguished. When a response from a particular analyte can be differentiated from other responses, that method is said to be selective. Very few examples exist in which a response from a single analyte can be isolated, that is, totally specific. Thus the term selectivity is used to the near exclusion of specificity.

In many techniques, especially spectroscopic detection, the analyst must choose which of several possible signals will be used. In general, the strongest signal would appear most likely (or at least the one giving rise to the best S/N), but, owing to the occurrence of interferences, it is not necessarily so. The ability of the technique to discriminate a given signal or set of signals from an undesirable signal is termed selectivity. The difficulty encountered in many real situations is interanalyte interactions (matrix effects). If matrix effects induce a response at the analyte signal position or contribute partially to the analyte signal, the quality of the measurement is degraded.

This problem is particularly important in spectral work involving condensed phases. The broad band nature of condensed phase spectra leads to overlapping of spectra from different analytes. Even in gas-phase spectroscopic studies, molecular bands can overlap, for example on atomic spectral lines. Close lying atomic spectral lines may overlap completely or partially. In such cases, high resolution monochromators may solve the problem. In pH measurements, alkali metal ions are bound to interfere. In emission spectroscopy, the radiation emitted by an analyte may be absorbed by another species in the matrix. Other expected interferants can include synthetic precursors, excipients, enantiomers, or degradation products.

Thus it is necessary to find the correct signal from the analyte. Observed signal, minus the correction, results in the working detectable signal. Corrections can be done in many ways. One method uses chemical reactions to “effectively” remove the interfering component by converting it to some innocuous form. Chemical treatment is also useful to convert the analyte to forms which are measurable. For example, Fe(III) can be converted to its highly colored thiocyanate complex (pretreatment), for which the concentration may be determined by colorimetry or spectrophotometry. In some cases, one may physically separate the interferent by a chromatographic technique or extraction.

Selectivity of an analyte can sometimes be enhanced along with sensitivity by derivatization (pretreatment). For example, in luminescence detection systems, the native luminescence intensity from an analyte may be too low for useful detection. In such cases, the molecule may be tagged with a fluorescent probe to produce a larger signal. This method is often employed in chromatography (to increase volatility by silylation, etc.) to separate closely eluting analytes and/or to detect the analytes (with fluoroprobes or UV detection). It should be noted that sample preservation methods may affect the choice of the pretreatment/sample preparation.
There are several ways in which to validate a technique's selectivity. For instance, during a chromatographic elution of a sample blank, the signal intensity from a region where a known analyte is expected to elute can be measured. The difference between the blank and the actual run will provide an indication of the selectivity of the technique toward that particular response. Secondly, the calibration curve for a particular analyte should have an intercept of zero representing no signal contribution at zero concentration. Any positive bias in the intercept value represents the lack of degree of analytical selectivity for that technique. Other techniques exist as well, e.g., acquiring spectra of the eluting species and checking for differences in the spectral profiles over the course of the peak elution.

The total number of applicable analytical techniques is so great that any attempt to be comprehensive is futile; however, a few main categories with common features can be identified. These categories are chromatography, spectroscopy, and electrochemistry. Of course, two or more can be combined in a single analysis. Each one of the main categories covers an enormous range of information and detail. Several books and book series have been written on these subjects. The purpose of Section 5 through 10 is to outline the main principles of the more instrumentally based categories, chromatography and spectroscopy.
5.0 REFERENCES


3. Ludwig Huber, Good Laboratory Practice and Good Manufacturing Practice - A Primer, 1994, Hewlett Packard Publication No. 12-5963-2115E.


36. HPLC for Environmental Analysis, 1994, Hewlett-Packard Publications, France, p. 44.


45. Stoeker, R.E. *Statistical Methods for Environmental Scientists*; J.A. Powell Publishing; Boulder, CO, 1995 [University of Denver: (303) 444-3979].
APPENDIX A

GROUND-WATER SAMPLING
GROUND-WATER SAMPLING

Introduction

Background

Ground-water sampling is conducted to provide information on the condition of subsurface water resources. Whether the goal of the monitoring effort is detection or assessment of contamination, the information gathered during sampling efforts must be of known quality and be well documented. The most efficient way to accomplish these goals is by developing a sampling protocol, which is tailored to the information needs of the program and the hydrogeology of the site or region under investigation. This sampling protocol incorporates detailed descriptions of sampling procedures and other techniques that, of themselves, are not sufficient to document data quality or reliability. Sampling protocols are central parts of networks or investigatory strategies.

The need for reliable ground-water sampling procedures has been recognized for years by a variety of professional, regulatory, public, and private groups. The technical basis for the use of selected sampling procedures for environmental chemistry studies has been developed for surface-water applications over the last four decades. Ground-water quality monitoring program, however, have unique needs and goals that are fundamentally different from previous investigative activities. The reliable detection and assessment of subsurface contamination require minimal disturbance of geochemical and hydrogeologic conditions during sampling.

At this time, proven well construction, sampling, and analytical protocols for ground-water sampling have been developed for many of the more problematic chemical constituents of interest. However, the acceptance of these procedures and protocols must await more careful documentation and firm regulatory guidelines for monitoring program execution. The time and expense of characterizing actual subsurface conditions place severe restraints on the methods that can be employed. Since the technical basis for documented, reliable drilling, sample collection, and handling procedures is in the early stages of development, conscientious efforts to document method performance under real conditions should be a part of any ground-water investigation (Barcelona and others, 1985; Scalf and others, 1981).

Information Sources

Much of the literature on routine ground-water monitoring methodology has been published in the last 10 years. The bulk of this work has emphasized ambient resource or contaminant resource monitoring (detection and assessment), rather than case preparation or enforcement efforts. General references that are useful to the design and execution of sampling efforts are the U.S. Geological Survey (1977), Wood (1976), the U.S. Environmental Protection Agency (Brass and others, 1977; Dunlap and others, 1977; Fenn and others, 1977; Sisk, 1981) and others (National Council of the Paper Industry, 1982; Tinlin, 1976). In large part, these works treat sampling in the context of overall monitoring programs, providing descriptions of available

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sampling mechanisms, sample collection techniques, and sample handling procedures. The impact of specific methodologies on the usefulness or reliability of the resulting data has received little discussion (Gibb and others, 1981).

High-quality chemical data collection is essential in ground-water monitoring programs. The technical difficulties involved in "representative" samplings have been recognized only recently (Gibb and others, 1981; Grisak and others, 1978). The long-term collection of high-quality ground-water chemistry data is more involved than merely selecting a sampling mechanism and agreeing on sample handling procedures. Efforts to detect and assess contamination can be unrewarding without accurate (i.e. unbiased) and precise (i.e., comparable and complete) concentration data on ground-water chemical constituents. Also, the expense of data collection and management argue for documentation of data quality.

Gillham and others (1983) published a very useful reference on the principal sources of bias and imprecision in ground-water monitoring results. Their treatment is extensive and stresses the minimization of random error, which can enter into well construction, sample collection, and sample handling operations. They further stress the importance of collecting precise data over time to maximize the effectiveness of trend analysis, particularly for regulatory purposes. Accuracy also is very important, since the ultimate reliability of statistical comparisons of results from different wells (e.g., upgradient versus downgradient samples) may depend on differences between mean values for selected constituents from relatively small replicate sample sets. Therefore, systematic error must be controlled by selecting proven methods for establishing sampling points and sample collection to ensure known levels of accuracy.

The Subsurface Environment
The subsurface environment may be categorized broadly into two zones, the unsaturated or vadose zone and the saturated zone. The use of the term "vadose" is more accurate because isolated saturated areas may exist in the unsaturated zone above the water table of unconfined aquifers.

Investigators have discovered recently that the subsurface is neither devoid of oxygen (Winograd and Robertson, 1982) nor sterile (Wilson and McNabb, 1983; Wilson and others, 1983). These facts may significantly influence the mobility and persistence of chemical species, as well as the transformations of the original components of contaminant mixtures (Schwarzenbach and others, 1985) that have been released to the subsurface.

The subsurface environment also is quite different from surface water systems in that vertical gradients in pressure and dissolved gas content have been observed within the usual depth ranges of monitoring interest (i.e., 1 to 150 m [3 to 500 ft]). In some cases, these gradients can be linked to well-defined hydrologic or geochemical processes. However, reports of apparently anomalous geochemical processes have increased in recent years, particularly at contaminated sites (Barcelona and Garske, 1983; Heaton and Vogel, 1981; Schwarzenbach and others, 1985; Winograd and Robertson, 1982; Wood and Petraitis, 1984).
The subsurface environment is not as readily accessible as surface water systems, and some disturbance is necessary to collect samples of earth materials or ground water. Therefore representative" (i.e., artifact or error free) sampling is really a function of the degree of detail needed to characterize subsurface hydrologic and geochemical conditions and the care taken to minimize disturbance of these conditions in the process (Claasen, 1982). Each well or boring represents a potential conduit for short-circuited contaminant migration or ground-water flow, which must be considered a potential liability to investigative activities.

The subsurface environment is dynamic over extended time frames and the processes of recharge and groundwater flow are very important to a thorough understanding of the system. Detailed descriptions of contaminant distribution, transport, and transformation necessarily rely on the understanding of basic flow and fluid transport processes. Short-term investigations may only provide a snapshot of contaminant levels or distributions. Since water-quality monitoring data are normally collected on discrete dates, it is very important that reliable collection methods are used to assure high data quality over the course of the investigation. The reliability of the methods should be investigated thoroughly during the preliminary phase of monitoring network implementation.

Although the scope of this discussion is on sampling ground water for chemical analysis, the same data quality requirements apply to water-level measurements and to hydraulic conductivity testing. These hydrologic determinations form the basis for interpreting chemical constituent data and may well limit the validity of fluid or solute transport model applications. Hydrologic measurements must be included in the development of the quality assurance/quality control (QA/QC) program for ground-water quality monitoring networks.

The Sampling Problem and Parameter Selection
Cost-effective water-quality sampling is difficult in ground-water systems because proven field procedures have not been extensively documented. Regulations that call for "representative sampling" alone are not sufficient to ensure high-quality data collection. The most appropriate monitoring and sampling procedures for a ground-water quality network will depend on the specific purpose of the program. Resource evaluation, contaminant detection, remedial action assessments, and litigation studies are purposes for which effective networks can be designed once the information needs have been identified. Due to the time, personnel needs, and cost of most water-quality monitoring programs, the optimal network design should be phased so as to make the most of the available information as it is collected. This approach allows for the gradual refinement of program goals as the network is implemented.

Two fundamental considerations are common to most ground-water quality monitoring programs: establishing individual sampling points (i.e., in space and time) and determining the elements of the water sampling protocol that will be sufficient to meet the information needs of the overall program. The placement and number of sampling points can be phased to gradually increase the scale of the monitoring program. Similarly, the chemical constituents of initial interest should provide background ground-water quality data from which a list of likely contaminants may be prepared as the program progresses. Table 1 shows candidate chemical and hydrologic parameters for both detective and assessment monitoring activities. Special care
should be taken to account for possible subsurface transformation of the principal pollutant species. Groundwater transport of contaminants can produce chemical distributions that vary substantially over time and space. In particular, transformation of organic compounds can change substantially the identity of the original contaminant mixture (Mackay and others, 1985; Schwarzenbach and others, 1985).

Detective Monitoring

Chemical Parameters*
- pH, \( \Omega^{-1} \), TOC, TOX, Alkalinity, TDS, Eh, Cl\(^-\), NO\(_3^-\), SO\(_4^{2-}\), PO\(_4^{3-}\), SiO\(_2\), Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), NH\(_4^+\), Fe, Mn

Hydrologic Parameters
- Water Level, Hydraulic Conductivity

Assessment Monitoring

Chemical Parameters*
- pH, \( \Omega^{-1} \), TOC, TOX, Alkalinity, TDS, Eh, Cl\(^-\), NO\(_3^-\), SO\(_4^{2-}\), PO\(_4^{3-}\), SiO\(_2\), B, Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), NH\(_4^+\), Fe, Mn, Zn, Cd, Cu, Pb, Cr, Ni, Ag, Hg, As, Sb, Se, Be

Hydrologic Parameters
- Water Level, Hydraulic Conductivity

\*\( \Omega^{-1} \) = specific conductance, a measure of the charged species in solution.

Table 1. Suggested Measurements for Ground-Water Monitoring Programs

Contaminant detection is generally the most important aspect of a water-quality program, and must be assured in network design. False negative contaminant readings due to the loss of chemical constituents or the introduction of interfering substances that mask the presence of the contaminants in water samples can be very serious. Such errors may delay needed remedial action and expose either the public or the environment to an unreasonably high risk. False positive observations of contaminants may call for costly remedial actions or more intensive study, which are not warranted by the actual situation. Thus, reliable sample collection and data interpretation procedures are central to an optimized network design. In this respect, monitoring in the vadose zone is attractive because it should provide an element of "early" detection capability. The methodologies available for this type of monitoring have been under development for some time. There are distinct limitations, however, to many of the available monitoring devices (Everett and McMillion, 1985; Everett and others, 1982; Wilson, 1981; Wilson, 1983), and it is frequently difficult to relate observed vadose zone concentrations quantitatively to actual contaminant distributions in ground water (Everett and others, 1984; Lindau and Spalding, 1984). Soil gas sampling techniques and underground storage task monitors have been commercially developed that can be extremely useful for source scouting. Given the complexity of vadose zone monitoring procedures and the need for additional
investigation (Robbins and Gemmell, 1985), implementing these techniques in routine groundwater monitoring networks may be difficult.

This chapter addresses water-quality sampling in the saturated zone, reflecting the advanced state of monitoring technology appropriate for this compartment of the subsurface. There are a number of useful reference materials for the development of effective ground-water sampling protocols, which include information on the types of drilling methods, well construction materials, sampling mechanisms, and sample handling methods currently available (Barcelona and others, 1985; Barcelona and others, 1983; Gillham and others, 1983; Scalf and others, 1981; Todd and others, 1976). To collect sensitive, high-quality contaminant concentration data, investigators must identify the type and magnitude of errors that may arise in ground-water sampling. Figure 1 presents a generalized diagram of the steps involved in sampling and the principal sources of error.

<table>
<thead>
<tr>
<th>Step</th>
<th>Sources of Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-Situ Condition</td>
<td></td>
</tr>
<tr>
<td>Establishing a Sampling Point</td>
<td>Improper well construction/ placement; inappropriate materials selection</td>
</tr>
<tr>
<td>Field Measurements</td>
<td>Instrument malfunction; operator error</td>
</tr>
<tr>
<td>Sample Collection</td>
<td>Sampling mechanism bias; operator error</td>
</tr>
<tr>
<td>Sample Delivery/Transfer</td>
<td>Sampling mechanism bias; sample exposure, degassing oxygenation; field conditions</td>
</tr>
<tr>
<td>Field Blanks, Standards</td>
<td>Operator error; matrix interferences</td>
</tr>
<tr>
<td>Field Determinations</td>
<td>Instrument malfunction; operator error; field conditions</td>
</tr>
<tr>
<td>Preservation/Storage</td>
<td>Matrix interferences; handling/labeling errors</td>
</tr>
<tr>
<td>Transportation</td>
<td>Delay; sample loss</td>
</tr>
</tbody>
</table>

*Figure 1. Steps and Sources of Error In Groundwater Sampling.*

Strict error control at each step is necessary for the collection of high-quality data representative of in situ conditions.
There are two major obstacles to controlling groundwater sampling errors. First, field blanks, standards, and split samples used in data quality assurance programs cannot account for changes that may occur in the integrity of samples prior to sample delivery to the land surface. Second, most of the sources of error that may affect sample integrity prior to delivery are not well documented in the literature for many of the contaminants of current interest. Among these sources of error are the contamination of the subsurface by drilling fluids, grouts, or sealing materials; the sorptive or leaching effects on water samples due to well casing; pump or sampling tubing materials' exposures; and the effects on the solution chemistry due to oxygenation, depressurization, or gas exchange caused by the sampling mechanism. These sources of error have been investigated to some extent for volatile organic contaminants under laboratory conditions. However, to achieve confidence in field monitoring and sampling instrumentation for routine applications, common sense and a "research" approach to regulatory monitoring may be needed. Two of the most critical elements of a monitoring program are establishing both reliable sampling points and simple, efficient sampling protocols that will yield data of known quality.

Establishing a Sampling Point

Taking adequate care in selecting drilling methods, well construction materials, and well development techniques should allow the approximation of representative groundwater sampling from a monitoring well. The representative nature of the water samples can be maintained consistently with a trained sampling staff and good field-laboratory communication. Also, important hydrologic measurements, such as water level and hydraulic conductivity, can be made from the same sampling point. A representative water sample may then be defined as a minimally disturbed sample taken after proper well purging, which will allow the determination of the chemical constituents of interest at predetermined levels of accuracy and precision. Sophisticated monitoring technology and sampling instrumentation are poor substitutes for an experienced sampling team that can follow a proven sampling protocol.

This section details some of the considerations in establishing a reliable sampling point. There are a number of alternative approaches for selecting a sampling point in monitoring network design, including deploying arrays of either nested monitoring wells or multilevel devices (Barvenik and Cadwgan, 1983; Pickens and others, 1978) at various sites within the area of interest. Different approaches have their individual merits, based on the ease of verifying sampling point isolation, durability, cost, ease of installation, and site-specific factors.

The most effective option for specific programs should be chosen with representative sampling criteria in mind. The sampling points must be durable, inert towards the chemical constituents of interest, allow for purging of stagnant water, provide sufficient water for analytical work with minimum disturbance, and permit the evaluation of the hydrologic characteristics of the formation of interest. Monitoring wells can be constructed to meet these criteria because a variety of drilling methods, materials, sampling mechanisms, and pumping regimes for sampling and hydrologic measurements can be selected to meet the current needs of most monitoring programs.
The placement and number of wells will depend on the complexity of the hydrologic setting and the degree of spatial and temporal detail needed to meet the goals of the program. Both the directions and approximate rates of ground-water movement must be known in order to satisfactorily interpret the chemical data. With this knowledge, it also may be possible to estimate the nature and location of pollutant sources (Gorelick and others, 1983). Subsurface geophysical techniques can be very helpful in determining the optimum placement of monitoring wells under appropriate conditions and when sufficient hydrogeologic information is available (Evans and Schweitzer, 1984). Well placement should be viewed as an evolutionary activity that may expand or contract as the needs of the program dictate.

**Well Design and Construction**

Effective monitoring well design and construction require considerable care and at least some understanding of the hydrogeology and subsurface geochemistry of the site. Preliminary borings, well drilling experience, and the details of the operational history of a site can be very helpful. Monitoring well design criteria include depth, screen size, gravel-pack specifications, and yield potential. These considerations differ substantially from those applied to production wells. The simplest, small diameter well completions that will permit development, accommodate the sampling gear, and minimize the need to purge large volumes of potentially contaminated water are preferred for effective routine monitoring activities. Helpful references include Barcelona and others (1983), Scalf and others (1981), and Wehrmann (1983).

**Well Drilling**

The selection of a particular drilling technique should depend on the geology of the site, the expected depths of the wells, and the suitability of drilling equipment for the contaminants of interest (see Chapter 1). Regardless of the technique used, every effort should be made to minimize subsurface disturbance. For critical applications, the drilling rig and tools should be steamcleaned to minimize the potential for cross-contamination between formations or successive borings. The use of drilling muds can be a liability for trace chemical constituent investigations because foreign organic matter will be introduced into the penetrated formations. Even "clay" muds without polymeric additives contain some organic matter, which is added to stabilize the clay suspension and may interfere with some analytical determinations. Table 2 contains information on the total and soluble organic carbon contents of some common drilling and grouting materials (Wood, 1976). The effects of drilling muds on ground-water solution chemistry have not been investigated in detail.

However, existing reports indicate that the organic carbon introduced during drilling can cause false water quality observations for long periods of time (Barcelona, 1984; Brobst, 1984). The fact that these interferences are observable for gross indicators of levels of organic carbon compounds (i.e., TOC) and reduced substances (i.e., COD) strongly suggests that drilling aids are a potential source of serious error. Special situations may call for innovative drilling techniques (Yare, 1975).

**Well Development, Hydraulic Performance, and Purging Strategy**

Once a well is completed, it is necessary to prepare the sampling point for water sampling and begin to evaluate the hydraulic characteristics of the producing zone. These steps provide a basis
for maintaining reliable sampling points. Over the duration of a ground-water monitoring program.

**Well Development.** The proper development of monitoring wells is essential to the collection of "representative" water samples. During the drilling process, fine particles are forced through the sides of the borehole into the formation, forming a mud cake that reduces the hydraulic conductivity of the materials in the immediate area of the well bore. To allow water from the formation being monitored to freely enter the monitoring well, this mud cake must be broken down opposite the well screen and the fine material removed from the well. This process also enhances the yield potential of the well, which is a critical factor when constructing monitoring wells in low-yielding geologic materials.

More importantly, monitoring wells must be developed to provide water free of suspended solids. When sampling for metal ions and other dissolved inorganic constituents, water samples must be filtered and preserved at the well site at the time of sample collection. Improperly developed monitoring wells will produce samples containing suspended sediments that may both bias the chemical analysis of the collected samples and cause frequent clogging of field filtering mechanisms. The additional time and money spent for well development will expedite sample filtration and result in samples that are more representative of water chemistry in the formation being monitored.

Development procedures used for monitoring wells are similar to those used for production wells. The first step in development involves the movement of water at alternately high and low velocity into and out of the well screen and gravel-pack to break down the mud cake on the well bore and loosen fine particles in the borehole. This step is followed by pumping to remove these materials from the well and the immediate area outside the well screen. This procedure should be continued until the water pumped from the well is visually free of suspended materials or sediments.

<table>
<thead>
<tr>
<th></th>
<th>Ash (% by wt)</th>
<th>Organic Content (% by wt)</th>
<th>Soluble Carbon (% by wt)</th>
<th>Soluble Carbon in Total Organic Content (% by wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Bentonite</em> muds/grouts</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volclay* (~90% montmorillonite)</td>
<td>92.2</td>
<td>1.8</td>
<td>&lt;0.001</td>
<td>94.4</td>
</tr>
<tr>
<td>Bensealence</td>
<td>88.5</td>
<td>11.5</td>
<td>&lt;0.001</td>
<td>3.7</td>
</tr>
<tr>
<td>&quot;Organic&quot; muds/drilling aids</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ez-Mud* (acrylamide-sodium acrylate copolymer dispersed in food-grade oil normally used in 0.25% dilution)</td>
<td>11.5</td>
<td>21.5</td>
<td>17.9</td>
<td>2.1</td>
</tr>
<tr>
<td>Reved* (guar bean starch-based mixture)</td>
<td>1.6</td>
<td>98.4</td>
<td>33.8</td>
<td>85.6</td>
</tr>
</tbody>
</table>

*All percentages determined on a moisture-free basis.
*Trademark of American Colloid Co.
*Trademark of NL Baroid/NL Industries Inc.
*Trademark of Johnson Division UOP Inc.

**Table 2. Composition of Selected Sealing and Drilling Muds**
Hydraulic Performance of Monitoring Wells.

The importance of understanding the hydraulics of the geologic materials at a site cannot be overemphasized. Collection of accurate water-level data from properly located and constructed wells provides information on the direction of ground-water flow. The success of a monitoring program also depends on knowledge of the rates of travel of both the groundwater and solutes. The response of a monitoring well to pumping also must be known to determine the proper rate and length of time of pumping prior to collecting a water sample.

Hydraulic conductivity measurements provide a basis for judging the hydraulic connection of the monitoring well and adjacent screened formation to the hydrogeologic setting. These measurements also allow an experienced hydrologist to estimate an optimal sampling frequency for the monitoring program (Barcelona and others, 1985).

Traditionally, hydraulic conductivity testing has been achieved by collecting drill samples, which were then taken to the laboratory for testing. Several techniques involving laboratory permeameters are routinely used. Falling head or constant head permeameter tests on recompressed samples in fixed wall or triaxial test cells are among the most common. The relative applicability of these techniques depends on both operator skill and methodology since calibration standards are not available. The major problem with laboratory test procedures is that the determined values are based on recompressed geologic samples rather than undisturbed geologic materials. Only limited work has been done to date on performing laboratory tests on "undisturbed" samples to improve the field applicability of laboratory hydraulic conductivity results. Melby (1989) reported that laboratory-determined values of hydraulic conductivity for cores of unconsolidated, fine-grained material from Oklahoma were three to six orders of magnitude smaller than values determined by aquifer testing. Considerable care must be exercised when evaluating laboratory-derived hydraulic conductivity coefficients.

Hydraulic conductivity is most effectively determined under field conditions by aquifer testing methods, such as pumping or slug testing (see Chapter 4). The water level drawdown can be measured during pumping.

Alternatively, water levels can be measured after the static water level is depressed by application of gas pressure or elevated by the introduction of a slug of water. These procedures are rather straightforward for wells that have been properly developed.

Well Purging Strategies.
The number of well volumes to be removed from a monitoring well prior to collecting a water sample must be tailored to the hydraulic properties of the geologic materials being monitored, the well construction parameters, the desired pumping rate, and the sampling methodology to be employed. No single number of well volumes to be pumped fits all situations. The goal in establishing a well purging strategy is to obtain water from the geologic materials being monitored while minimizing the disturbance of the regional flow system and the collected sample. To accomplish this goal, a basic understanding of well hydraulics and the effects of pumping on the quality of water samples is essential. Water that has remained in the well casing
more than about 2 hours has had the opportunity to exchange gases with the atmosphere and to interact with the well casing material. Therefore, the chemistry of water stored in the well casing is not representative of that in the aquifer and should not be collected for analysis. Purge volumes and pumping rates should be evaluated on a case-by-case basis.

Gibb (1981) has shown how the measurements of hydraulic conductivity can be used to estimate the well purging requirement. Figures 2 and 3 show an example of this procedure. In practice, it may be necessary to test the hydraulic conductivity of several wells within a network. The calculated purging requirement should then be verified by measurements of pH and specific conductance during pumping to signal equilibration of the water being collected.

The selection of purging rates and volumes of water to be pumped prior to sample collection also can be influenced by the anticipated water quality. In hazardous environments where purged water must be contained and disposed of in a permitted facility, it is desirable to minimize this amount. This can be accomplished by pumping the wells at very low pumping rates (100 mL/min) to minimize the drawdown in the well and maximize the percentage of aquifer water delivered to the surface in the shortest period of time. Pumping at low rates, in effect, isolates the column of stagnant water in the well bore and negates the need for its removal. This approach is only valid in cases where the pump intake is placed at the top of, or in, the well screen.

In summary, well purging strategies should be established by (1) determining the hydraulic performance of the well; (2) calculating reasonable purging requirements, pumping rates, and volumes based on hydraulic conductivity data, well construction data, site hydrologic conditions, and anticipated water quality; (3) measuring the well purging parameters to verify chemical "equilibrated"conditions; and (4) documenting the entire effort (actual pumping rate, volumes pumped, and purging parameter measurements before and after sample collection).

Given:

48-foot deep, 2-inch diameter well
2-foot long screen
3-foot thick aquifer
static water level about 15 feet below land surface
hydraulic conductivity = $10^{-2}$ cm/sec

Assumptions:
A desired purge rate of 500 mL/min and sampling rate of 100 mL/min will be used.

Calculations:

One well volume = (48 ft - 15 ft) x 613 mL/ft (2-inch diameter well)
= 20.2 liters

Aquifer Transmissivity = hydraulic conductivity x aquifer thickness
= $10^{-2}$ m/sec x 1 meter
= $10^{-2}$ m$^2$/sec or 8.64 m$^3$/day

From Figure 2-2b:
At 5 minutes: 95% aquifer water and (5 min x 0.5 L/min)/20.2 L
= 0.12 well volumes
At 10 minutes: 100% aquifer water and (10 min x 0.5 L/min)/20.2 L
= 0.24 well volumes

It appears that a high percentage of aquifer water can be obtained within a relatively short time of pumping at 500 mL/min$^{-1}$. This pumping ratio is below that used during well development to prevent well damage or further development.

Figure 2. Example of Well Purging Requirement Estimating Procedure (Barcelona and others, 1985)
Figure 3. Percentage of Aquifer Water Versus Time for Different Transmissivities

Sampling Materials and Mechanisms.
In many monitoring situations, it is not possible to predict the requirements that either materials for well casings, pumps, and tubing, or pumping mechanisms must meet in order to provide error-free samples of ground water. Ideally, these components of the system should be durable and inert relative to the chemical properties of samples or the subsurface so as to neither contaminate nor remove chemical constituents from the water samples. Due to the long duration of regulatory program requirements, well casing materials, in particular, must be sufficiently durable and nonreactive to last several decades. It is generally much easier to substitute more appropriate sampling pumps or pump/tubing materials as knowledge of subsurface conditions improves than to drill additional wells to replace inadequate well casing or screen materials. Also, there is no simple way to account for errors that occur prior to handling a sample at the land surface. Therefore, it is good practice to carefully choose the components of the sampling system that make up the rigid materials in well casing/screens or pumps, and the flexible materials used in sample delivery tubing.

Rigid Materials. An experienced hydrologist can base well construction details mainly on hydrogeologic criteria, even in challenging situations where a separate contaminant phase may be present (Villaume, 1985). However, the best material for a specific monitoring application must be selected by considering subsurface geochemistry and the likely contaminants of interest. Therefore, strength, durability, and inertness should be balanced with cost considerations in the choice of rigid materials for well casing, screens, pumps, etc. (see Chapter 1).

Common well casing materials include TFE (Teflon®), PVC (polyvinyl chloride), stainless steel, and other ferrous materials. The strength, durability, and potential for sorptive or leaching interferences with chemical constituents have been reviewed in detail for these materials.
(Barcelona and others, 1985; Barcelona and others, 1983). Unfortunately, there is very little documentation of the severity or magnitude of well casing interferences from actual field investigations. This is the point at which optimized monitoring network design takes on an element of "research," as the components of the monitoring installation will need to be systematically evaluated.

Polymeric materials have the potential to absorb dissolved chemical constituents and leach either previously sorbed substances or components of the polymer formulations. Similarly, ferrous materials may adsorb dissolved chemical constituents and leach metal ions or corrosion products, which may introduce errors into the results of chemical analysis. This potential in both cases is real, yet not completely understood. The recommendations in the references noted above can be summarized as follows:

Teflon® is the well casing material least likely to cause significant error in ground-water monitoring programs focused on either organic or inorganic chemical constituents. It has sufficient strength for most applications at shallow depth (i.e., < 100 m) and is among the most inert materials ever made. For deeper installations, it can be linked to another material above the highest seasonal water level.

Stainless steel (either 316 or 304 type) well casing, under noncorrosive conditions, is the second least likely material to cause significant error for organic chemical constituent monitoring investigations. Fe, Mn, or Cr may be released, under corrosive conditions. Organic constituent sorption effects also may provide significant sources of error after corrosion processes have altered the virgin surface.

Rigid PVC well casing material that has National Sanitation Foundation approval should be used in monitoring well applications when noncemented or threaded joints are used, and organic chemical constituents are not expected to be of either present or future interest. Significant losses of strength, durability and inertness (i.e., sorption or leaching) may be expected under conditions where organic contaminants are present in high concentration. PVC should, however, perform adequately in inorganic chemical constituent studies when concentrations of organic constituents are not high and tin or antimony species are not being targeted.

Monitoring wells made of appropriate materials and screened over discrete sections of the saturated thickness of geologic formations can yield a wealth of chemical and hydrologic information. Whether or not this level of performance is achieved frequently may depend on the care taken in evaluating the hydraulic performance of the sampling point.

Flexible Materials: Pump components and sample delivery tubing may contact a water sample more intimately than other components of a sampling system, including storage vessels and well casing. Similar considerations of inertness and noncontaminating properties apply to tubing, bladder, gasket and seal materials. Experimental evidence (Barcelona and others, 1985) has supported earlier recommendations drawn from manufacturers' specifications (Barcelona and others, 1983). A summary is provided in Table 3. Again, the care taken in materials' selection for
Materials Recommendations

<table>
<thead>
<tr>
<th>Materials</th>
<th>Recommendations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polytetrafluoroethylene (Teflon*)</td>
<td>Recommended for most monitoring work, particularly for detailed organic analytical schemes. The material least likely to introduce significant sampling bias or imprecision. The easiest material to clean in order to prevent cross-contamination.</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>Strongly recommended for corrosive high dissolved solids solutions. Less likely to introduce significant bias into analytical results than polymer formulations (PVC) or other flexible materials with the exception of Teflon*.</td>
</tr>
<tr>
<td>Polyethylene (linear)</td>
<td>Not recommended for detailed organic analytical schemes. Plasticizers and stabilizers make up a sizable percentage of the material by weight as long as it remains flexible. Documented interferences are likely with several priority pollutant classes.</td>
</tr>
<tr>
<td>PVC (flexible)</td>
<td>Flexible elastomeric materials for gaskets, O-rings, bladder, and tubing applications. Performance expected to be a function of exposure type and the order of chemical resistance as shown. Recommended only when a more suitable material is not available for the specific use. Actual controlled exposure trials may be useful in assessing the potential for analytical bias.</td>
</tr>
<tr>
<td>Viton*</td>
<td></td>
</tr>
<tr>
<td>Silicone (medical grade only)</td>
<td></td>
</tr>
<tr>
<td>Neoprene</td>
<td></td>
</tr>
</tbody>
</table>

* Trademark of DuPont, Inc.

Table 3. Recommendations for Flexible Materials in Sampling Applications

the specific needs of the sampling program can pay real dividends and provides greater assurance of error-free sampling.

Sample Mechanisms. It is important to remember that sampling mechanisms themselves are not protocols. The sampling protocol for a particular monitoring network is basically a step-by-step written description of the procedures used for well purging, delivering samples to the surface, and handling samples in the field. Once the protocol has been developed and used in a particular investigation, it provides a basis for modifying the program, if the extent or type of contamination requires more intensive work. An appropriate sampling mechanism is, however, an important part of any protocol. Ideally, the pumping mechanism should be capable of purging the well of stagnant water at rates of liters or gallons per minute and also of delivering groundwater to the surface so that sample bottles may be filled at low flow rates (i.e., about 100 mL/min⁻¹) to minimize turbulence and degassing of the sample. In this way the criteria for representative sampling can be met while keeping the purging and sample collection steps simple. Nielsen and Yeates (1985) reviewed the types of sample collection mechanisms commercially available (Anonymous, 1985). This review supports the results, of research studies of their performance (Barcelona and others, 1984; Stoltzenburg and Nichols, 1985). Figure 4 shows examples of types of pumps or other samplers, which are fully described in a number of
Figure 4. Schematic Diagrams of Common Groundwater Sampling Devices (Neilsen and Yeates, 1985)
references (Barcelona and others, 1985; Gillham and others, 1983; Scalt and others, 1981). Given all of the varied hydrogeologic settings and potential chemical constituents of interest, several types of pumps or sampling mechanisms may be suitable for specific applications. Figure 5 contains some recommendations for reliable sampling mechanisms relative to the sensitivity of the sample to error. The main criteria for sampling pumps are the capabilities to purge stagnant water from the well and to deliver the water samples to the surface with minimal loss of sample integrity. Clearly, a mechanism that is shown to provide accurate and precise samples for volatile organic compound determinations should be suitable for most chemical constituents of interest.

After establishing a sampling point and the means to collect a sample, the next step is the development of the detailed sampling protocol.

Elements of the Sampling Protocol
There are few aspects of this subject that generate more controversy than the sampling steps, which make up the sampling protocol. Efforts to develop reliable protocols and optimize sampling procedures require particular attention to sampling mechanism effects on the integrity of ground-water samples (Barcelona and others, 1984; Stolzenburg and Nichols, 1985), as well as to the potential errors involved in well purging, delivery tubing exposures (Barcelona and others, 1985; Ho, 1983), sample handling, and the impact of sampling frequency on both the sensitivity and reliability of chemical constituent monitoring results. Quality assurance measures, including field blanks, standards, and split control samples, cannot account for errors in these steps of the sampling protocol. Actually, the sampling protocol is the focus of the overall study network design (Nacht, 1983), and it should be prepared flexibly so that it can be refined as information on site improves.

Each step within the protocol has a bearing on the quality and completeness of the information being collected. This is perhaps best shown by the progression of steps depicted in Figure 6. Corresponding to each step is a goal and recommendation for achieving that goal. The principal utility of this description is that it provides an outlined agenda for high-quality chemical and water-quality data.

To ensure maximum utility of the sampling effort and resulting data, it is essential to document the sampling protocol as performed in the field. In addition to noting the obvious information (i.e., persons conducting the sampling, equipment used, weather conditions, adherence to the protocol, and unusual observations), three basic elements of the sampling protocol should be recorded: (1) water-level measurements made prior to sampling, (2) the volume and rate at which water is removed from the well prior to sample collection (well purging), and (3) the actual sample collection, including measurement of well-purging parameters, sample preservation, sample handling, and chain of custody.

Water-Level Measurement
Prior to well purging or sample collection, it is extremely important to measure and record the water level in the well. These measurements are needed to estimate the amount of water to be purged prior to sample collection. Likewise, this information can be useful when interpreting monitoring results. Low water levels may reflect the influence of the cone of depression.
surrounding a nearby production well. High water levels, compared to measurements made at other times of the year, may be indicative of recent recharge events. In relatively shallow settings, high water levels from recent natural recharge events may result in the increase of certain constituents leached from the unsaturated zone or in the dilution of the dissolved solids content in the collected sample.

Documenting the nonpumping water levels for all wells at a site will provide historical information on the hydraulic conditions at the site. Analysis of this information may reveal changes in flow paths and serve as a check on the effectiveness of the wells to monitor changing hydrologic conditions. It is very useful to develop an understanding of the seasonal changes in water levels and associated chemical concentration variability at the monitored site.

<table>
<thead>
<tr>
<th>Type of constituent</th>
<th>Example of constituent</th>
<th>Positive displacement bladder pumps</th>
<th>Thief, in situ or dual check valve bailers</th>
<th>Mechanical positive displacement pumps</th>
<th>Gas-drive devices</th>
<th>Suction mechanisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile Organic Compounds</td>
<td>Chloroform TOX CH₂Hg</td>
<td>Superior performance for most applications</td>
<td>May be adequate if well purging is assured</td>
<td>May be adequate if design and operation are controlled</td>
<td>Not recommended</td>
<td>Not recommended</td>
</tr>
<tr>
<td>Organometallics</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dissolved Gases</td>
<td>O₂, CO₂ pH, Ω⁻¹ Eh</td>
<td>Superior performance for most applications</td>
<td>May be adequate if well purging is assured</td>
<td>May be adequate if design and operation are controlled</td>
<td>Not recommended</td>
<td>Not recommended</td>
</tr>
<tr>
<td>Well-purging Parameters</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trace Inorganic Metal Species</td>
<td>Fe, Cu NO₂⁻, S⁻</td>
<td>Superior performance for most applications</td>
<td>May be adequate if well purging is assured</td>
<td>Adequate</td>
<td>May be adequate</td>
<td>May be adequate if materials are appropriate</td>
</tr>
<tr>
<td>Reduced Species</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Major Cations and Anions</td>
<td>Na⁺, K⁺, Ca²⁺ Mg²⁺ Cl⁻, SO₄⁻</td>
<td>Superior performance for most applications</td>
<td>Adequate</td>
<td>Adequate</td>
<td>Adequate</td>
<td>Adequate</td>
</tr>
</tbody>
</table>

Figure 5. Matrix of Sensitive Chemical Constituents and Various Sampling Mechanisms
<table>
<thead>
<tr>
<th>Step</th>
<th>Goal</th>
<th>Recommendations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrologic Measurements</td>
<td>Establish nonpumping water level.</td>
<td>Measure the water level to ± 0.3 cm (± 0.01 ft).</td>
</tr>
<tr>
<td>Well Purging</td>
<td>Remove or isolate stagnant H$_2$O which would otherwise bias representative samples</td>
<td>Pump water until well purging parameters (e.g., pH, T, Ω$^{-1}$, Eh) stabilize to ±10% over at least two successive well volumes pumped.</td>
</tr>
<tr>
<td>Sample Collection</td>
<td>Collect samples at land surface or in well-bore with minimal disturbance of sample chemistry</td>
<td>Pumping rates should be limited to ~100 mL/min for volatile organics and gas-sensitive parameters.</td>
</tr>
<tr>
<td>Filtration/Preservation</td>
<td>Filtration permits determination of soluble constituents and is a form of preservation. It should be done in the field as soon as possible after collection.</td>
<td>Filter: Trace metals, inorganic anions/cations, alkalinity. Do not filter: TOC, TOX, volatile organic compound samples; other organic compound samples only when required.</td>
</tr>
<tr>
<td>Field Determination</td>
<td>Field analysis of samples will effectively avoid bias in determining parameters/constituents which do not store well; e.g., gases, alkalinity, pH.</td>
<td>Sample for determining gases, alkalinity and pH should be analyzed in the field if at all possible.</td>
</tr>
<tr>
<td>Field Blanks/Standards</td>
<td>These blanks and standards will permit the correction of analytical results for changes which may occur after sample collection: preservation, storage, and transport.</td>
<td>At least one blank and one standard for each sensitive parameter should be made up in the field on each day of sampling. Spiked samples are also recommended for good QA/QC.</td>
</tr>
<tr>
<td>Sample Storage/Transport</td>
<td>Refrigerate and protect samples to minimize their chemical alteration prior to analysis.</td>
<td>Observe maximum sample holding or storage periods recommended by the Agency. Documentation of actual periods should be carefully performed.</td>
</tr>
</tbody>
</table>

Figure 6. Generalized Ground-Water Sampling Protocol.
Purging

The volume of stagnant water that should be removed from the monitoring well should be calculated from the analysis of field hydraulic conductivity measurements. Rule-of-thumb guidelines for the volume of water to be purged can cause time delays and unnecessary pumping of excess contaminated water. These rules (i.e., 3-, 5-, or 10-well volumes) largely ignore the hydraulic characteristics of individual wells and geologic settings. One advantage of using the same pump to both purge stagnant water and collect samples is the ability to measure pH and specific conductance in an in-line flow cell. These parameters aid in verifying the purging efficiency and also provide a consistent basis for comparing samples from a single well or wells at a particular site. Since pH is a standard variable for aqueous solutions that is affected by degassing and depressurization (i.e., loss of CO₂), in-line measurements provide more accurate and precise determinations than discrete samples collected by grab sampling mechanisms.

The following example illustrates some of the other advantages of verifying the purge requirement for monitoring wells.

Documentation of the actual well purging process employed should be a part of a standard field sampling protocol. The calculated well purging requirement (e.g., >90 percent aquifer water) calls for the removal of five well volumes prior to sample collection. Field measurements of the well purging parameters have historically confirmed this recommended procedure. During a subsequent sampling effort, 12 well volumes were pumped before stabilized well purging parameter readings were obtained. Several possible causes could be explored: (1) a limited plume of contaminants may have been present at the well at the beginning of sampling and inadvertently discarded while pumping in an attempt to obtain stabilized indicator parameter readings; (2) the hydraulic properties of the well may have changed due to silting or encrustation of the screen, indicating the need for well rehabilitation or maintenance; (3) the flow-through device used for measuring the indicator parameters may have been malfunctioning; or (4) the well may have been tampered with by the introduction of a contaminant or relatively clean water in an attempt to bias the sample results.

Sample Collection and Handling

Water samples should be collected when the solution chemistry of the ground water being pumped has stabilized as indicated by pH, Eh, specific conductance, and temperature readings.

In practice, stable sample chemistry is indicated when the purging parameter measurements have stabilized over two successive well volumes. First, samples for volatile constituents, TOC, TOX, and those constituents that require field filtration or field determination should be collected. Then large-volume samples for extractable organic compounds, total metals, or nutrient anion determinations should be collected.

All samples should be collected as close as possible to the well head. A "tee" fitting placed ahead of the in-line device for measuring the well purging parameters makes this more convenient. Regardless of the sample mechanism in use or the components of the sampling train, wells that are located upgradient of a site, and therefore are expected to be representative of background quality, should be sampled first to minimize the potential for cross-contamination. Laboratory
detergent solutions and distilled water should be used to clean the sampling train between samples. An acid rinse (0.1 N HCl) or solvent rinse (i.e., hexane or methanol) may be used to supplement these cleaning steps, if necessary. Cleaning procedures should be followed by distilled water rinses, which may be saved to check cleaning efficiency.

The order in which samples are taken for specific types of chemical analyses should be decided by the sensitivity of the samples to handling (i.e., most sensitive first) and the need for specific information. For example, the flowchart shown in Figure 7 depicts a priority order for a generalized sample collection effort. The samples for organic chemical constituent determinations are taken in decreasing order of sensitivity to handling errors, while the inorganic chemical constituents, which may require filtration, are taken afterwards.

Instances arise, even with properly developed monitoring wells, that call for the filtration of water samples. It should be evident, however, that adequate well development procedures, which require 2 to 3 hours of bailing, swabbing, pumping, or air purging at each well, may save many hours in sample filtration. Well development may have to be repeated at periodic intervals to minimize the collection of turbid samples. In this respect, it is important to minimize the disturbance of fines that accumulate in the well bore. This can be achieved by careful placement of the sampling pump intake at the top of the screened interval, low pumping rates, and avoiding the use of bailing techniques that disturb sediment accumulations.

It is advisable to refrain from filtering TOC, TOX, or other organic compound samples because the increased handling required may result in the loss of chemical constituents of interest. Allowing any fine material to settle prior to analysis, followed by decanting the sample, is preferable to filtration in these instances. If filtration is necessary for the determination of extractable organic compounds, it should be performed in the laboratory using nitrogen pressure. When samples must be filtered, it may be necessary to run parallel sets of filtered and unfiltered samples with standards to establish the recovery of hydrophobic compounds. All of the materials' precautions used in the construction of the sampling train should be observed for filtration apparatus. Vacuum filtration of groundwater samples is not recommended.

Water samples for dissolved inorganic chemical constituents (e.g., metals, alkalinity, and anionic species) should be filtered in the field. The preferred arrangement is an in-line filtration module, which utilizes sampling pump pressure for its operation. These modules have tubing connectors on the inlet and outlet parts and range in diameter from 2.5 to 15 cm. Large diameter filter holders, which can be rapidly disassembled for filter pad replacement, are the most convenient and efficient designs (Kennedy and others, 1976; Skougstad and Scarbo, 1968).

Representative sampling results from the execution of a carefully planned sampling protocol. An important consideration for maintaining sample integrity after collection is to minimize sample handling, which may bias subsequent determinations of chemical constituents. Since opportunities to collect high-quality data for the characterization of site conditions may be limited by time, it is
prudent to conduct sample collection as carefully as possible from the beginning of the sampling period. It is preferable to risk error on the conservative side when doubt exists as to the sensitivity of specific chemical constituents to sampling or handling errors. Repeat sampling or analysis cannot make up for lost data collection opportunities.

For samples collected for specific chemical constituents, recommended sample handling and analysis procedures may need to be modified. Samples that contain several chemicals and have undergone extended storage periods can cause significant problems. It is frequently more effective to perform a rapid field determination of specific inorganic constituents (e.g., alkalinity, pH, ferrous iron, sulfide, nitrite, or ammonium) than to attempt sample preservation followed by laboratory analysis of these samples.

**Quality Assurance/Quality Control**
Planning for valid water-quality data collection depends upon both the knowledge of the system and continued refinement of all sample handling/collection procedures.

As discussed earlier, the need to begin QA/QC planning with the installation of the sampling point cannot be overemphasized.
<table>
<thead>
<tr>
<th>Parameters (Type)</th>
<th>Volume Required (mL)</th>
<th>Container (Material)</th>
<th>Preservation Method</th>
<th>Maximum Holding Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well Purging</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH (grab)</td>
<td>50</td>
<td>T, S, P, G</td>
<td>None; field det.</td>
<td>1 hr**</td>
</tr>
<tr>
<td>Ω&lt;sup&gt;-1&lt;/sup&gt; (grab)</td>
<td>100</td>
<td>T, S, P, G</td>
<td>None; field det.</td>
<td>1 hr**</td>
</tr>
<tr>
<td>T (grab)</td>
<td>1000</td>
<td>T, S, P, G</td>
<td>None; field det.</td>
<td>None</td>
</tr>
<tr>
<td>Eh (grab)</td>
<td>1000</td>
<td>T, S, P, G</td>
<td>None; field det.</td>
<td>None</td>
</tr>
<tr>
<td>Contamination indicators</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH, Ω&lt;sup&gt;-1&lt;/sup&gt; (grab)</td>
<td>As above</td>
<td>As above</td>
<td>As above</td>
<td>As above</td>
</tr>
<tr>
<td>TOC</td>
<td>40</td>
<td>G, T</td>
<td>Dark, 4°C</td>
<td>24 hr</td>
</tr>
<tr>
<td>TOX</td>
<td>500</td>
<td>G, T</td>
<td>Dark, 4°C</td>
<td>5 days</td>
</tr>
<tr>
<td>Water Quality</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dissolved gases</td>
<td>10 mL minimum</td>
<td>G, S</td>
<td>Dark, 4°C</td>
<td>&lt;24 hr</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;, CH&lt;sub&gt;4&lt;/sub&gt;, CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkalinity/Acidity</td>
<td>100</td>
<td>T, G, P</td>
<td>4°C/None</td>
<td>&lt;6 hr**/&lt;24 hr</td>
</tr>
<tr>
<td>(Fe, Mn, Na&lt;sup&gt;+&lt;/sup&gt;, K&lt;sup&gt;+&lt;/sup&gt;, Ca&lt;sup&gt;+&lt;/sup&gt;, Mg&lt;sup&gt;2+&lt;/sup&gt;)</td>
<td>All filtered 1000 mL</td>
<td>T, P</td>
<td>Field acidified to pH</td>
<td>6 months**</td>
</tr>
<tr>
<td>(PO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-3&lt;/sup&gt;, Cl&lt;sup&gt;-&lt;/sup&gt;, Silicate)</td>
<td>@50</td>
<td>(T, P, G glass only)</td>
<td>4°C</td>
<td>24 hr/7 days;</td>
</tr>
<tr>
<td>NO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>100</td>
<td>T, P, G</td>
<td>4°C</td>
<td>24 hr</td>
</tr>
<tr>
<td>SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>50</td>
<td>T, P, G</td>
<td>4°C</td>
<td>7 days</td>
</tr>
<tr>
<td>NH&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
<td>400</td>
<td>T, P, G</td>
<td>4°C/H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt; to pH &lt;2</td>
<td>24 hr/7 days</td>
</tr>
<tr>
<td>Phenols</td>
<td>500</td>
<td>T, G</td>
<td>4°C/H&lt;sub&gt;3&lt;/sub&gt;PO&lt;sub&gt;4&lt;/sub&gt; to pH &lt;4</td>
<td>24 hr</td>
</tr>
<tr>
<td>Drinking Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Suitability</td>
<td>Same as above for</td>
<td>Same as above</td>
<td>Same as above</td>
<td>6 months</td>
</tr>
<tr>
<td></td>
<td>water quality cations</td>
<td>above</td>
<td>above</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As, Ba, Cd, Cr, Pb,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hg, Se, Ag</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F&lt;sup&gt;-&lt;/sup&gt;</td>
<td></td>
<td>Same as chloride</td>
<td>Same as above</td>
<td>7 days</td>
</tr>
<tr>
<td>Remaining Organic Parameters</td>
<td>As for TOX/TOC, except where analytical method calls for acidification of sample</td>
<td></td>
<td></td>
<td>24 hr</td>
</tr>
</tbody>
</table>

* It is assumed that at each site, for each sampling date, replicates, a field blank and standards must be taken at equal volume to those of the samples.

** Temperature correction must be made for reliable reporting. Variations greater than ±10% may result from longer holding period.

*** In the event that HNO<sub>3</sub> cannot be used because of shipping restrictions, the sample should be refrigerated to 4°C, shipped immediately, and acidified on receipt at the laboratory. Container should be rinsed with 1:1 HNO<sub>3</sub> and included with sample.

Note: T = Teflon; S = Stainless steel; P = PVC, polypropylene, polyethylene; G = borosilicate glass. From Scalf et al., 1981.

Table 4. Recommended Sample Handling and Preservation Procedures for a Detective Monitoring Program
The use of field blanks, standards, and spiked samples for field QA/QC planning with the installation of the sampling point cannot be overemphasized.

The use of field blanks, standards, and spiked samples for field QA/QC performance is analogous to the use of laboratory blanks, standards, and procedural or validation standards. The fundamental goal of field QC is to ensure that the sample protocol is being executed faithfully and that situations that might lead to error are recognized before they seriously impact the data. The use of field blanks, standards, and spiked samples can account for changes in samples that occur during laboratory blanks, standards, and procedural or sample collection.

Field blanks and standards enable quantitative correction for bias (i.e., systematic errors), which arise due to handling, storage, transportation, and laboratory procedures. Spiked samples and blind controls provide the means to correct combined sampling and analytical accuracy or recoveries for the actual conditions to which the samples have been exposed.

All QC measures should be performed for at least the most sensitive chemical constituents for each sampling date. Examples of sensitive constituents would be benzene or trichloroethylene as volatile organic compounds and lead or iron as metals. It is difficult to use laboratory blanks alone for determining the limits of detection or quantitation. Laboratory distilled water may contain apparently higher levels of volatile organic compounds (e.g., methylene chloride) than would uncontaminated groundwater samples. The field blanks and spiked samples should be used for this purpose, conserving the results of lab blanks as checks on elevated laboratory background levels.

Whether or not the groundwater is contaminated with interfering compounds, spiked samples provide a basis for both identifying the constituents of interest and correcting their recovery (or accuracy) based on the recovery of the spiked standard compounds. For example, if trichloroethylene in a spiked sample is recovered at a mean level of 80 percent (~20 percent bias), the concentrations of trichloroethylene determined in the samples for this sampling date may be corrected by a factor of 1.2 for low recovery. Similarly, if 50 percent recovery (~50 percent bias) is reported for the spiked standard, it is likely that sample handling or analytical procedures are out of control and corrective measures should be taken at once. It is important to know whether the laboratory has performed these corrections or taken corrective action when it reports the results of analyses. It should be further noted that many regulatory agencies require evidence of QC and analytical performance but do not generally accept data that have been corrected.

Field blanks, standards, and blind control samples provide independent checks on handling and storage, as well as the performance of the analytical laboratory. Ground-water analytical data are incomplete unless the analytical performance data (e.g., accuracy, precision, detection, and quantitation limits) are reported with each set of results. Discussions of whether groundwater quality has changed significantly must be tempered by the accuracy and precision performance for specific chemical constituents.

Table 5 is a useful guide to the preparation of field standards and spiking solutions for split samples. It is important that the field blanks and standards are made on the day of sampling and
are subjected to all conditions to which the samples are exposed. Field spiked samples or blind controls should be prepared by spiking with concentrated stock standards in an appropriate background solution prior to the collection of any actual samples. Additional precautions should be taken against the depressurization of samples during air transport and the effects of undue exposure to light during sample handling and storage. All of the QC measures noted above will provide both a basis for high-quality data reporting and a known degree of confidence in data interpretation. Well-planned overall quality control programs also will minimize the uncertainty in long-term trends when different personnel have been involved in collection and analysis.

Sample Storage and Transport
The storage and transport of ground-water samples often are the most neglected elements of the sampling protocol. Due care must be taken in sample collection, field determinations, and handling. Transport should be planned so as not to exceed sample holding time before laboratory analysis. Every effort should be made to inform the laboratory staff of the approximate time of arrival so that the most critical analytical determinations can be made within recommended storage periods. This may require that sampling schedules be adjusted so that the samples arrive at the laboratory during working hours.

The documentation of actual sample storage and treatment may be handled by chain of custody procedures. Figure 8 shows an example of a chain of custody form. Briefly, the chain of custody record should contain the dates and times of collection, receipt, and completion of all the analyses on a particular set of samples. Frequently, it is the only record that exists of the actual storage period prior to the reporting of analytical results. The sampling staff members who initiate the chain of custody should require that a copy of the form be returned to them with the analytical report. Otherwise, verification of sample storage and handling will be incomplete.

Shipping should be arranged to ensure that samples are neither lost nor damaged enroute to the laboratory. Several commercial suppliers of sampling kits permit refrigeration by freezer packs and include proper packing. It may be useful to include special labels or distinctive storage vessels for acid-preserved samples to accommodate shipping restrictions.

Summary
Groundwater sampling is conducted for a variety of reasons, ranging from detection or assessment of the extent of a contaminant release to evaluations of trends in regional water quality. Reliable sampling of the subsurface is inherently more difficult than either air or surface water sampling because of the inevitable disturbances that well drilling or pumping can cause and the inaccessibility of the sampling zone. Therefore, "representative" sampling generally requires minimal disturbance of the subsurface environment and the properties of a representative sample are scale dependent. For any particular case, the applicable criteria should be set at the beginning of the effort to judge representativeness.
### Table 5. Field Standard and Sample Spiking Solutions

Reliable sampling protocols are based on the hydrogeologic setting of the study site and the degree of analytical detail required by the monitoring program. Quality control begins with the evaluation of the hydraulic performance of the sampling point or well and the proper selection of mechanisms and materials for well purging and sample collection. All other elements of the program and variables that affect data validity may be accounted for by field blanks, standards, and control samples.

Although research is needed on a host of topics involved in groundwater sampling, defensible sampling protocols can be developed to ensure the collection of data of known quality for many types of programs. If properly planned and developed, long-term sampling efforts can benefit from the refinements that research progress will bring. Careful documentation will provide the key to this opportunity.
CHAIN OF CUSTODY RECORD

Sampling Date ___________________ Site Name ____________________
Well or Sampling Points: ________________________________________

Sample Sets for Each: Inorganic, Organic, Both.
Inclusive Sample Numbers:
Company’s Name __________________________ Telephone (__) __________
Address __________________________________________________________________
number street city state zip
Collector’s Name ________________________ Telephone (__) __________
Date Sampled ___________ Time Started _________ Time Completed _________
Field Information (Precautions, Number of Samples, Number of Sample Boxes, Etc.):
1. _____________________________________________________________
   name organization location
2. _____________________________________________________________
   name organization location
Chain of Possession (After samples are transported off-site or to laboratory):
1. _____________________________________________________________ (IN)
   signature title
   name (printed) date/time of receipt (OUT)
2. _____________________________________________________________ (IN)
   Signature Title
   Name (Printed) Date/time of receipt (OUT)

Analysis Information:
Analysis Begun Analysis Completed
Aliquot (date/time) initials (date/time) initials
1. 
2. 
3. 
4. 
5. 

Figure 8. Sample Chain of Custody Form

REFERENCES

Anonymous, 1985, Monitoring products, a buyers guide: Ground Water Monitoring Review,
v. 5, no. 3, pp. 33–45.


Brobst, R.B., 1984, Effects of two selected drilling fluids on ground water sample chemistry: in Monitoring Wells, Their Place in the Water Well Industry Educational Session, NWWA National Meeting and Exposition, Las Vegas, NV.


Sisk, S.W., 1981, NE/C manual for groundwater/ subsurface investigations at hazardous waste sites: U.S. Environmental Protection Agency, Office of Enforcement, National Enforcement Investigations Center, Denver, CO.


APPENDIX B

CHROMATOGRAPHY PRINCIPLES
INTRODUCTION

The essential goal in chromatography is to effect a spatial separation of the individual chemical species in a sample. Thus the term "separation science" has become a synonym for chromatography. Chromatography involves the transport of a controlled amount of sample through a length of adsorbing material. The mechanism of transport is a fluid flow (e.g., a carrier gas in gas chromatography, an eluting solvent in liquid chromatography) through the adsorbing material. Analytes exhibit different degrees of adsorption to a chosen adsorbing material. If a component of the mixture (a solute) is adsorbed weakly onto the surface of the solid stationary phase, it will travel down the column faster than another solute that is more strongly adsorbed. The eluting components require a distinct amount of time to follow the length of the medium (relative to the time of sample injection). Comparison of the retention times for unknown samples with those for standards provides the basis for compound identification. The desired reproducibility of retention times requires that the samples be loaded with an initially narrow spatial extent and that the adsorbing material conditions (temperature, pressure, column packing) be held uniform and reproducible. Various detectors are available for analyte detection and quantification.

The elements that are found in any chromatographic system include the support, the stationary phase, the mobile phase, the sample injection system, and the detection system. Overviews of gas chromatography and high-performance liquid chromatography are shown in Figures 1 and 2. An illustration, however, is drawn from column chromatography. The

![Diagram](image)

Figure 1. Experimental layout of a gas chromatographic instrument. Column lengths typically used are in the 1–100-meter range.
support in column chromatography is a glass tube of small diameter (3–10 mm) compared to its length (5–20 cm), the stationary phase is a material such as silica gel or alumina packed as uniformly as possible into the tube, the mobile phase is a solvent flowing vertically under the influence of gravity through the tube, the injection "system" is loading the sample by pouring it onto the top of the column, and the detection system is visual observation of colored bands of components as they move through the column. In thin-layer chromatography, the support is a glass or metal plate, the stationary phase is a thin layer of alumina or similar inert material on the support, and the mobile phase is a solvent, in this case moving upward through capillary action. Samples are "injected" by spotting them onto the stationary phase, and detection is once again visual using a UV lamp or by using iodine vapor to darken faint spots.

The main goal in chromatography methods development is in finding the optimal set of conditions to achieve a necessary degree of separation and quantitation performance. Optimization is not trivial since several criteria must be balanced, including the degree of resolution (separation of one component from another), the minimal detection mass, and the overall analysis time. Many experimental parameters can be varied over a continuous range, resulting in a number of combinations of conditions that can be used. For example, gas chromatography (GC) and high-performance liquid chromatography (HPLC) require selection of the column adsorbing material (chemical constitution and particle size), column length, and column diameter. Selection of the flow rate of the mobile phase (carrier gas) and the column temperature is also necessary. Column temperature may be changed during the run according to a preset program or held fixed. HPLC requires the choice of a solvent (or mixture of solvents for
elution) which can be crucial for successful separation. The eluting solvent mixture can be continuously varied (not necessarily in linear fashion) to improve resolution of complex mixtures. This method is referred to as gradient elution.

Chromatographic identification of a compound is usually made by noting the time interval between injection and detection. If conditions are constant for each injection, the rate of travel of a compound along the column is highly reproducible. The time interval between sample injection and specific compound detection is referred to as the retention time of that compound. The analogous parameter in thin-layer chromatography is the $R_f$ factor, which is the ratio of the component travel to that of the travel of the solvent front. Retention times and $R_f$ factors are sensitive to the conditions of the experiment, so standards must be run frequently to verify performance. The plot of detector signal vs. time is termed the “chromatogram.” The number of peaks in the chromatogram will indicate the number of separated bands (ideally equal to the number of analytes). The areas under the peaks (or peak heights) are proportional to the amount of the analyte. Unfortunately, the relationship between peak area and concentration generally varies too much with detector conditions to allow a direct determination. Standards must be run to establish the proportionality factor.

The greatest strength of chromatographic methods is their specificity/selectivity in achieving features that can be reliably ascribed to individual analytes. For complex samples with many components, e.g., gasoline, retention time may not provide a sufficiently specific identification, owing to uncertainties in retention times. In such cases, the standard detectors can be replaced or paired with chemically specific detection schemes such as mass spectrometry, infrared spectroscopy, and UV spectroscopy. Reference is then made to “hyphenated techniques” such as GC-MS, and GC–FT-IR. This practice can be taken to great lengths. For example, the combination of gas chromatography with the eluant frozen in an argon matrix for later examination by infrared spectroscopy is known as GC–MS–FT-IR analysis. Another approach involves a multidimensional chromatography, in which the material eluting over a given time range is subjected to a secondary separation in a different column.

The basis of chromatographic quantitation is the comparison of peak heights and peak areas with standards. Solutions of known composition (number of analytes and their concentrations) are injected and their retention times and peak heights and areas of the eluting components noted. When the unknown is run, retention times are compared to the standard, and concentrations are then determined by relative peak heights and peak areas. The standardization procedure also serves to define the dynamic range, sensitivity, and precision of the analysis (the precision of the analysis having impact on the accuracy of the analysis).

An internal standard is a substance that is added to the sample at the earliest possible point in an analytical scheme to compensate for sample losses occurring during sample preparation and final chromatographic analysis.

Chromatographic specificity is generally obtained at the expense of analysis time. Retention times can be as short as a few seconds for simple and relatively concentrated mixtures (certain air samples, for example). However, satisfactory analysis of complex samples with
analytes present at trace levels may require conditions that lead to retention times of many minutes or even hours. The more similar the physicochemical properties of the compounds to be separated, the closer the retention times. Achieving improved resolution through the use of longer columns, injecting less sample onto the column, or reduction of the flow rate of the mobile phase results in longer retention times and, hence, longer analysis times.

Many samples require pretreatment or special handling before injection. Chromatography generally relies on analysis of a fluid sample. There is a great demand for the analysis of volatile organic compounds (VOCs), which are often dissolved in environmental water samples. Aqueous solutions and solids are not usually injected into a gas chromatograph. The analytes are dissolved/extracted into a volatile solvent or transferred to the gas phase. Extraction methods differ for liquids and solids with the exception of purge and trap (PT) which will overlap. PT, heated headspace (HH), liquid–liquid extraction (LLE), supercritical fluid extraction (SFE), Soxhlet, sonication and microwave-assisted extraction are the most frequently utilized means to transfer analytes from one phase to another. Another reason for sample pretreatment is to remove materials that might temporarily or permanently plug the column.

The sample may require manipulation prior to the analysis to get the analyte within the range of concentration for which the chosen analytical technique is reliable. Chromatographic techniques can often analyze extremely small amounts of sample (ng to pg). Only small volumes can be injected. One ng in 1 μL is still 1 mg/L, a comparatively high concentration. Thus preconcentration steps are often employed in chromatography. In the most desirable situation, the sample is twice the concentration and gives twice the signal. This is a linear technique. Hence, one finds reference to the linear dynamic range (LDR) of a technique (Section 4.2). The optimal LDRs are linear over concentration ranges of 5 orders of magnitude or more. It may also be necessary to dilute the sample to bring it into linear range.

**Gas Chromatography**

GC is the standard laboratory technique for volatile and semivolatile organic analysis. The basis of GC is that the sample is transported by a gas through a column. Since analytes exhibit differential adsorption to the column-packing material, the time required to pass through the column will vary. If the column conditions (primarily temperature and flow rate) are standardized, the retention time will provide a means of identification.

There are innumerable variations; when there are several analytes of interest, it is likely that one or more of the analytes are outside the calibration range, so dilutions and additional injections are usually required. With complex samples, there is often overlap between peaks that have similar retention times.

Direct sample injection with GC is usually not possible. Because of the complexities of sample preparation and the nature of the experiment, standards are required on a regular basis. The main options for sample introduction are PT, HH, solid-phase extraction (SPE), direct injection following LLE, or SFE. PT is the EPA-recommended procedure for analysis of VOCs. A good discussion of HH, LLE, and SFE may be found in Bruno and Ely. Table 6
(Section 5.2.4) lists the means of detection and optimization of detection methods for general or specific analytes.

Compounds that lack sufficient vapor pressure at room temperature are volatized immediately after injection through a heated injection port to a heated sample chamber. If the sample is thermally labile or truly nonvolatile, it is still possible to analyze it via GC by derivatizing it to a volatile species prior to sample injection. The samples are injected through a self-sealing septum via a microliter syringe. The injection port is heated to ensure adequate volatilization of the sample. As the analytes are swept through the column by the carrier gas, they partition between the moving gas and the stationary phase. Because different analytes exhibit different partition coefficients, they move away (separate) from one another via the carrier gas. The analytes will leave the column at the other end as separate “bands.” The analytes leaving the column are detected with an analyte-sensitive detector or a universal detector. The detector signal is monitored as a function of time.

Extraction Techniques

Static Headspace Analysis. Static headspace analysis involves placement of the liquid or solid sample in a suitable vial that has been sealed with a Teflon-lined silicone septum. A thermostated equilibrium is established in which the volatile components are distributed between the sample and the gaseous space above the sample (headspace). The sampling of the headspace can be undertaken using a syringe with manual control or with an electropneumatic dosing system. Manual syringe methods are generally not as accurate for analysis since they are prone to user error, expansion of the headspace pressure into the needle volume, and absorption of headspace gases by the syringe. Use of gas-lock mechanisms and internal standards can alleviate many of the difficulties associated with manual syringe techniques. Automated pneumatic sampling devices are an advantage when large quantities of sample are to be analyzed.

Unlike the manual method, automated pneumatic procedures provide for constant volume and pressure sampling. Pressure constancy is achieved in the headspace through use of an inert gas that is of equal pressure to the inlet source. At this point, the gas is injected into the column or thermostated sample loop for later transfer. Typical headspace volumes are 0.5–3.0 mL which can be used in conjunction with packed columns. If a capillary column is employed this volume represents too great a load and will result in a severely broad injection band with loss of chromatographic resolution. In this case, flow splitting is used to rapidly transfer a fraction of the sample to the column. Since only a fraction of the injected vapor is analyzed, this method results in loss of sensitivity. Loss of sensitivity can be circumvented by using cold traps or cold fingers to condense the volatile vapors prior to the head of the column.

Dynamic Headspace Analysis. Dynamic headspace analysis involves the continuous flow of extraction gas over the liquid or solid sample, subsequently trapping volatiles using solid-phase extraction or a cold-trapping scheme. Tenax material backed up with a silica gel, carbon, or coated stationary phase is used to improve the trapping efficiency.
The PT, gas-phase stripping, or gas-phase sparging procedure involves the extraction gas being slowly bubbled through the liquid or solid sample. This method is employed in situations that require analysis of low-concentration volatiles or matrices that have a high affinity for volatiles, i.e., high partition coefficient.

Cold trapping is advantageous since thermally labile and polar compounds are generally not affected during the trapping process. Another advantage of cold trapping is the limitation of undesirable chromatographic peaks (resulting from artifact species).

Determination of the concentrations of VOCs in aqueous solution is a commonplace concern of the gas industry. BTEX compounds (benzene, toluene, ethylbenzene, xylenes), chlorinated solvents, and alkanes are commonly the subject of environmental regulations and are well suited for PT analysis. During PT analysis, 5–10 mL of aqueous solution is sparged (bubbled) with an inert gas, usually helium. The bubbling action aids the transfer of the volatiles via the gas phase into the trap. The sparge gas flow is terminated after approximately 10 minutes (time is predetermined). The trap is then heated to a temperature sufficient for desorption of the analytes. A small volume of headspace containing the VOC vapors is introduced into the column for separation. Each of these steps is carried out automatically with modern PT accessories.

Table 1 lists standard VOCs that are conventionally measured by PT. There are four classifications of VOCs: BTEX, chlorinated solvents, halomethanes, and alkanes. PT is unsuitable for semivolatile organic compounds (large aromatic hydrocarbons) and polar compounds that are not easily sparged from aqueous solution. It is possible to apply PT to methanol solutions, but the solubility of many organic compounds limits applicability.

The PT method is susceptible to contamination from high-concentration samples. Samples may contain one or more analytes at concentrations several times greater than the linear dynamic range of the instrument. The overloaded system must be thoroughly cleaned of purgeable organics and the cleanout verified by blank runs — a costly and time-consuming process.

Columns

*Packed Columns.* Packed columns are a common mode of GC analyte separation. The spatial separation of components is achieved with a liquid stationary phase coated onto inert particles of uniform size (i.e., 100/120 mesh). The loading of the liquid on the inert material is usually 3%–4% by mass. The coated material is packed into a long tube of narrow cross section (2–12-ft length and 2–4-mm ID) made of glass or stainless steel. A stream of the mobile carrier gas, usually nitrogen or helium, is “pumped” into the GC column, which is heated in an oven. Temperature control of the column is automated. Some packed GC columns have a solid stationary phase. Commonly used stationary phases are silicon gums or fluids (SE-30, OV-1, OV101, etc.) and glycol succinates. Finely divided and chemically treated fire brick particles are often used for the support (Chromosorb T, Chromosorb WHT). Characteristics of typical GC columns are outlined in Table 2.
**TABLE 1**

Selective Volatile Organic Compounds and Their Properties

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol. Weight</th>
<th>Solubility (in methanol)</th>
<th>Vapor Pressure, torr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>58</td>
<td>miscible</td>
<td>270 (@ 30°C)</td>
</tr>
<tr>
<td>Benzene</td>
<td>78</td>
<td>1780</td>
<td>76</td>
</tr>
<tr>
<td>Bromodichloromethane</td>
<td>164</td>
<td>7500</td>
<td>50</td>
</tr>
<tr>
<td>Bromoform</td>
<td>253</td>
<td>3190 (@ 30°C)</td>
<td>6 (@ 25°C)</td>
</tr>
<tr>
<td>Bromomethane</td>
<td>95</td>
<td>900</td>
<td>1250</td>
</tr>
<tr>
<td>2-Butanone</td>
<td>72</td>
<td>270,000</td>
<td>76</td>
</tr>
<tr>
<td>Carbon Disulfide</td>
<td>76</td>
<td>2300</td>
<td>260</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>154</td>
<td>800</td>
<td>90</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>113</td>
<td>500</td>
<td>9</td>
</tr>
<tr>
<td>Chloroethane</td>
<td>65</td>
<td>5740</td>
<td>1000</td>
</tr>
<tr>
<td>2-Chloroethylvinyl Ether</td>
<td>107</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>120</td>
<td>8000</td>
<td>160</td>
</tr>
<tr>
<td>Chloromethane</td>
<td>51</td>
<td>8348</td>
<td>3800</td>
</tr>
<tr>
<td>Dibromochloromethane</td>
<td>208</td>
<td>3300</td>
<td>15 (@ 10.5°C)</td>
</tr>
<tr>
<td>1,2-Dichlorobenzene</td>
<td>147</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>1,3-Dichlorobenzene</td>
<td>147</td>
<td>123 (@ 25°C)</td>
<td>1</td>
</tr>
<tr>
<td>1,4-Dichlorobenzene</td>
<td>147</td>
<td>49 (@ 22°C)</td>
<td>1</td>
</tr>
<tr>
<td>1,1-Dichloroethane</td>
<td>99</td>
<td>5500</td>
<td>180</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>99</td>
<td>8690</td>
<td>61</td>
</tr>
<tr>
<td>1,1-Dichloroethene</td>
<td>97</td>
<td>400</td>
<td>500</td>
</tr>
<tr>
<td><em>trans</em>-1,2-Dichloropropane</td>
<td>97</td>
<td>600</td>
<td>200 (@ 14°C)</td>
</tr>
<tr>
<td>1,2-Dichloropropane</td>
<td>113</td>
<td>2700</td>
<td>42</td>
</tr>
<tr>
<td><em>cis</em>-1,3-Dichloropropene</td>
<td>110</td>
<td>2700</td>
<td>34 (@ 25°C)</td>
</tr>
<tr>
<td><em>trans</em>-1,3-Dichloropropene</td>
<td>111</td>
<td>2800</td>
<td>43 (@ 25°C)</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>106</td>
<td>152</td>
<td>7</td>
</tr>
<tr>
<td>2-Hexanone</td>
<td>100</td>
<td>3500</td>
<td>2</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>85</td>
<td>20,000</td>
<td>349</td>
</tr>
<tr>
<td>Methylisobutylketone</td>
<td>100</td>
<td>17,000</td>
<td>6</td>
</tr>
<tr>
<td>Perchloroethylene</td>
<td>166</td>
<td>150</td>
<td>14</td>
</tr>
<tr>
<td>Styrene</td>
<td>104</td>
<td>300</td>
<td>5</td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>168</td>
<td>2900</td>
<td>5</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>166</td>
<td>150</td>
<td>18 (@ 25°C)</td>
</tr>
<tr>
<td>Toluene</td>
<td>92</td>
<td>515</td>
<td>22</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>133</td>
<td>4400</td>
<td>100</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>133</td>
<td>4500</td>
<td>19</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>132</td>
<td>700</td>
<td>60</td>
</tr>
<tr>
<td>Trichlorofluoromethane</td>
<td>137</td>
<td>1100 (@ 25°C)</td>
<td>687</td>
</tr>
<tr>
<td>Vinyl Acetate</td>
<td>86</td>
<td>25,000</td>
<td>115 (@ 25°C)</td>
</tr>
<tr>
<td>Vinyl Chloride</td>
<td>63</td>
<td>1100 (@ 25°C)</td>
<td>2660 (@ 25°C)</td>
</tr>
<tr>
<td>Total Xylenes</td>
<td>106</td>
<td>198</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 2

Characteristics of Typical GC Columns

<table>
<thead>
<tr>
<th>Variable</th>
<th>FSOT</th>
<th>WCOT</th>
<th>SCOT</th>
<th>Packed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length, m</td>
<td>10–100</td>
<td>10–100</td>
<td>10–100</td>
<td>16</td>
</tr>
<tr>
<td>Inside Diameter, mm</td>
<td>0.1–0.53</td>
<td>0.25–0.75</td>
<td>0.5</td>
<td>2–4</td>
</tr>
<tr>
<td>Efficiency, plates/m</td>
<td>2000–4000</td>
<td>1000–4000</td>
<td>600–1200</td>
<td>500–1000</td>
</tr>
<tr>
<td>Capacity, ng</td>
<td>10–75</td>
<td>10–1000</td>
<td>10–1000</td>
<td>10–10^6</td>
</tr>
<tr>
<td>Relative Pressure</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Relative Speed</td>
<td>Fast</td>
<td>Fast</td>
<td>Fast</td>
<td>Slow</td>
</tr>
<tr>
<td>Chemical Inertness</td>
<td>Best</td>
<td>No</td>
<td>No</td>
<td>Poor</td>
</tr>
<tr>
<td>Flexible</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>

1 Fused-silica, open tubular column (capillary).
2 Wall-coated, open tubular column (packed).
3 Support-coated, open tubular column.

Capillary Columns. In capillary GC the open capillary tubes are made of fused silica with 0.2–0.4-mm ID. The liquid phase is coated onto the inner wall of the capillary. Another way of using capillaries involves the use of porous layer, open tubular (PLOT) columns, also known as SCOT. Here the inner wall of the column is made porous, and the liquid is loaded onto the porous layer. Capillary columns offer better separation efficiencies than packed columns because of the absence of eddy currents, lower loading, lower loss of liquid phase during the operation, and ability to use longer tubes.

Sample Injection. Sample injection in capillary GC is less straightforward than in packed column GC. Care must be taken to avoid overloading the column. The split injection technique uses about 1%–10% of the vaporized sample, with the remaining 90%–99% vented out of the system. Splitless injection vaporizes the sample and condenses it at the head of the column. By using a solvent or by changing temperature, the analytes are concentrated at the head of the column, helping to rid the sample of the solvent. The vapor above the sample is directly injected onto the column in headspace analysis. Volatile analytes can be preconcentrated on an absorbent like Tenax using the PT method. The absorbed material can then be desorbed straight into the column by heating.

Temperature and Pressure Programming

Complex samples often contain analytes that travel through the column at very different rates, eluting some analytes quickly but retaining others and broadening their peaks. Increasing the temperature of the column after the elution of the less tightly held analytes will hasten the release of the more strongly held components into the mobile (gas) phase, thus avoiding the
problem of broadening. The temperature may be increased in one step to a specific high value or may be ramped at a regular rate (linear), exponential, logarithmic, or as some combination of these patterns. Temperature changes are controlled by a computer/microprocessor. Figure 3 shows a comparison of the relative time differences between the chromatographic peaks of a mixture separated at different temperatures.

Pressure can also be changed according to a specified pattern. This technique is useful for thermally sensitive analytes. It is noted that an optimal flow rate exists for a given system, and changing the flow rate beyond (or below) the optimum value results in lower resolution. Flow rate and temperature programming can be combined to optimize analytical specificity, selectivity, and dynamic range.

Figure 3. Temperature-dependent gas chromatograms of the same analytical mixture: a) 45°C (isothermal), b) 145°C (isothermal), c) 30°–180°C (programmed).
Detectors

The three main characteristics of GC detectors highlighted in this discussion are sensitivity, selectivity, and dynamic range.

There is a significant range in detector sensitivity among the various GC detectors (Figure 4). A quick review shows that ion-generated detection schemes have a pronounced and consistently higher level of sensitivity. However, many of the less sensitive techniques like the thermal conductivity detector (TCD) offer compensating characteristics which make their use worthwhile. The versatility of GC detectors lies in their selectivity. GC detectors can be universal, selective, or specific in the kinds of analytes that they detect:

- Electron capture detector (ECD)
- Electron capture detector for chlorine (ELCD[Cl])
- Flame ionization detector (FID)
- Flame photometric detector with P: phosphorus and S: sulfur (FPD)
- Nitrogen phosphorus detector for nitrogen (NPD [N])
- Nitrogen phosphorus detector for phosphorus (NPD[P])
- Photoionization detector (PID)
- Thermal conductivity detector (TCD)

**Universal Detectors.** Universal detectors, by definition, generally detect anything which elutes from the chromatographic column. Two common universal detectors are the TCD and total ion monitoring by GC/MS. The overall sensitivities of these techniques can often pose a problem if chromatographic resolution of complex mixtures interferes with the detection of the desired analyte. The operational disadvantages of universal detectors include response to column bleed (i.e., detection

![Comparison of the sensitivities of gas chromatographic detectors.](image)

Figure 4. Comparison of the sensitivities of gas chromatographic detectors.
of column matrix material) and detection of small changes in the temperature and pressure of the
carrier gas.

Selective Detectors. Selective detectors are sensitive to selective elements, chemical functional
groups, and structural or differentiating properties of analytes. The thermionic detector is selective to
organic compounds that contain nitrogen and phosphorus. The ECD is selective to halogenated
compounds and the electrolytic conductivity detector is selective to halogens, nitrogen, and sulfur.
NPD(N) and NPD(P) are selective for nitrogen and phosphorus, respectively, and ELCD(Cl) is
selective for chlorine.

Flame Ionization Detector. The FID (Figure 5) is the most commonly used GC detector. The
gas effluent from a GC passes into a small hydrogen flame. As the organic molecules “burn” in the
hydrogen flame, a small fraction are broken into ionic fragments that can be accumulated at an
electrode collector and detected as a current. The magnitude of the current produced is proportional to
the quantity of the analyte sampled. The shape of the ionization flame and the nearness of the flame to
the collector electrode directly impact detector sensitivity.

Specific Detectors. Specific detectors are highly selective. The three most common specific
detectors are the FPD, MSD, and FT-IR. The FPD scheme uses narrow wavelength filtering after
analyte combustion and emission to selectively detect phosphorus (FPD(P))-or sulfur (FPD(S))-containing compounds.

There are two broad categories of GC detection: charged particle detection and neutral analyte
detection. Detection with charged particles (electrons and positive ions) is extremely sensitive. The
paths of charged particles can be manipulated with electric and magnetic fields. Collection
efficiencies of nearly 100% are possible. The most popular detectors for GC rely on charged particle
collection, differing primarily in terms of how the ions are created. Molecular ions are higher energy
forms of the neutrals. The energy difference between the ground (lowest energy) state of the neutral
and the ground state of the positive ion is referred to as the ionization energy (sometimes referred to
as the ionization potential). The ionization energy is the energy that must be supplied to remove an
electron from the neutral species. Ionization energies for most organic molecules fall in the range
8–12 eV. Nonionic detectors rely principally on specific physicochemical properties of the analyte of
interest.

Detector Types. The standard detectors for GC are TCDs and FIDs. The less commonly used
detectors and various hyphenated techniques are discussed in the next section.

Thermal Conductivity Detector. TCD detection is a universal, nondestructive, commonly used
scheme by which the thermal conductivity properties of an eluting analyte are used as a means of
detection. The TCD measures the difference in thermal conductivity between the carrier gas, usually
helium, and the analytes. Helium is most commonly used because of its high thermal conductivity,
although hydrogen, nitrogen, and argon can be implemented. Thus, as an eluting analyte band crosses
the detector threshold, a change in thermal conductivity occurs and is measured. The actual detection
mechanism consists of a heated filament held under constant applied voltage with a given resistance.
Filaments have been made from tungsten, gold-plated metals, and tungsten–rhenium. Filaments can
be coated with a metal oxide layer to reduce their chemical interactions with analytes and are, hence, referred to as passivated filaments. As analytes pass over the heated filament, the different thermal conductivities give rise to differences in the amount of heat removed from the filament surface, leading to changes in filament resistance. Change is measured as detector response. Some TCDs vary in this regard by measuring the changes in resistance, while maintaining a constant filament temperature with analyte flow.

The basic principle behind flow modulation (Figure 6) is the ability to quickly switch the flow passing over the filament detector. By switching, or modulating the flow between carrier gas and column effluent, a single filament can be used for quasi-continuous measurement of the response from the carrier gas and the eluting analytes. In the left diagram, the flow past the detector filament arises from the column effluent. A signal measurement is taken at this time. In the right diagram, the flow is switched, and the detector filament is flushed with carrier gas. After the switch, when carrier gas resides in the detector cell, a reference measurement is taken. This measurement represents the signal of the baseline. The difference in signal values between both of these steps represents the net signal. The modulation of flows occurs on the order of 100 milliseconds.

There are several practical concerns which are relevant to TCD operations. Two primary considerations include the flow rate of the carrier gas and proper setting of the block temperature. Often a compromise is required between the boiling points of analytes and the degree of detector sensitivity and filament lifetime. While higher temperatures (300°–400°C) maintain volatility of the analyte species, such conditions decrease filament sensitivity and create harsh reactive conditions which lower the filament lifetime. Losses in sensitivity approaching a factor of six with an increase from 200°–400°C are common.

TCDs are universal since nearly all molecular species exhibit detectable differences in their thermal conductivity over helium. TCDs are ideal for hydrocarbon analysis of small chain hydrocarbons as well as many of the heavier hydrocarbon BTEX species which can be run at relatively low temperatures (60°–120°C).

FIDs are particularly well suited to organic analysis of species which readily ionize in the hydrogen/air flame — the response being fairly linear to every CH unit in a molecule. FIDs are sensitive to a wide range of organic hydrocarbons that directly impact fuel, power, and environmental fields. In this area they can often produce good quantification with much less calibration and are easy to operate. However, responses from H₂O, CO₂, N₂, O₂, CS₂, formaldehyde, and heavily halogenated compounds are generally poor, therefore making the FID a selective detector option. For optimal use, FIDs must be fine-tuned with respect to hydrogen, air, and carrier gas flow rates. Since water is formed in the combustion process, the detector temperature must be set high enough to prevent condensation on the collector electrode assembly. Silica from GC columns and certain derivatizing agents can leave deposits on the detector assembly. Condensation and deposits can lead to decreased sensitivity and increased detector corrosion.
Figure 5. (Top) Carrier gas passes over the filament and maintains a constant temperature while the resistant is measured. (Bottom) Flow diagram of a commercially available TCD cell. Note the switching of flow and its effect on column effluent flow through the filament channel.

Figure 6. Overviews of the FID. Note the requirement that the detection zone be placed above the base of the flame to properly detect ions after combustion.
**Electron Capture Detector.** ECDs are commonly used for the selective detection of polyhalogenated hydrocarbons; e.g., analysis of pesticides which often contain a variety of halogenated constituents. They are also used in other environmental analyses. ECDs operate on the principle that a radioactive source, usually nickel-63, creates beta emissions which ionize the carrier gas and create free electrons in the detector chamber (Figure 7). These free electrons are driven to a pulsed anode and detected by a change in the current flowing from the anode. When electrophilic polyhalogenated species are introduced into the detector volume, many of these free electrons are captured. The voltage pulse applied to the anode is generally short enough to allow the remaining free electrons to hit the anode and result in current flow. The mass of the polyhalogenated ion impedes its flow to the anode. It is flushed from the system by the movement of the carrier gas before any contact can be made with the anode and is not detected. The result is an effective decrease in overall current flow arising from the constant ionization of beta emissions. This effective decrease in current is recorded as the signal of the analyte passing through the detector.

The constant, yet gradual change in sensitivity over a range of organic types is an interesting property of the ECD which arises from its selective application to polyhalogenated organics (Table 3). Note the near 1-millionfold difference in ECD response between hydrocarbons and the polyhalogenated species. Because of the great selectivity of this technique, monochloronated compounds, (e.g., 1-chlorobutane), can often be used in the analyte extraction while having minimal effects on the chromatogram. The need for very pure and dry carrier gases (nitrogen or 4% methane in argon; 99.9995% purity), along with minimal column bleed and system leaks, is crucial for successful ECD operation.

![Diagram of ECD](image_url)

Figure 7. (Top) Movement of electrons during the voltage pulse applied by the ECD. (Bottom) ECD.
TABLE 3

ECD Response to Various Compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Relative Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbons</td>
<td>1</td>
</tr>
<tr>
<td>Ethers, Esters</td>
<td>10</td>
</tr>
<tr>
<td>Aliphatic Alcohols, Ketones, Amines, Monochlorine, Monofluorine Compounds</td>
<td>100</td>
</tr>
<tr>
<td>Monobromide, Dichloride, and Difluoride Compounds</td>
<td>1,000</td>
</tr>
<tr>
<td>Anhydrides and Trichloride Compounds</td>
<td>10,000</td>
</tr>
<tr>
<td>Monoiodine Dibromide, Polychlorine and Polyfluoride Compounds</td>
<td>100,000</td>
</tr>
<tr>
<td>Diiodine, Tribromide, Polychloride, and Polyfluoride Compounds</td>
<td>1,000,000</td>
</tr>
</tbody>
</table>

Organochlorine compounds, especially chlorinated solvents and freons, PCBs, halogenated alkenes and alkanes, are compounds which are commonly analyzed with ECDs.

**Thermionic or Nitrogen Phosphorus Detector.** The NPD is similar in appearance to the ECD, but operationally different. A differentiating factor is the presence of an alkali salt, potassium or rubidium, positioned above the column outlet which serves as a source of ionization (Figure 8). The placement of the thermionic salt near the column outlet, along with the use of minimal air and hydrogen flows, selectively ionizes organic compounds containing N and P. The ions are collected by a negatively charged electrode and registered as a change in current flow.

This method has gained widespread acceptance as a trace analysis technique for the detection of compounds containing N and P. Operationally, thermionic detection is very sensitive to variations in gas flows. Special care is required to assure that all glassware is acid-washed and free of any phosphate detergents which would interfere with the analysis. Chlorinated solvents and silanizing compounds can harm the alkali salt source and decrease the lifetime of the detector. Noise (rapid changes of the signal during its recording, i.e., spikes) is a particular concern if liquid phases containing nitrogen are used, if phosphoric acid-treated columns are employed, or even if vapors such as cigarette smoke are present.

The NPD is used in pharmaceutical and clinical areas in applications where therapeutic levels of drugs are often too low for use with FID. NPDs have also found special applications in pesticide analyses.

**Flame Photometric Detector.** The FPD (Figure 9) is based on the chemiluminescence of phosphorus- and sulfur-containing hydrocarbon fragments produced in a hydrogen/air flame. Analytes are introduced into the flame and converted to excited S=S molecules (sulfur) or excited HPO molecules (phosphorus). Chemical reactions within the flame produce these species in a metastable state. As these states decay, photons specific to these species are released. A filter is incorporated to
Figure 8. View of the column exit port in a nitrogen phosphorus detector. Rubidium and cesium salts are typically used for both N and P analysis, while sodium and potassium are used for P analysis.

remove undesirable background signals, after which the photons are detected and amplified by a photomultiplier tube.

Like several of the detectors discussed so far, the FPD requires a degree of expertise and care for optimal performance. It is noted that reactions of sulfur in the flame give rise to emitted light, with an intensity proportional to the square of the sulfur atom concentration. If hydrocarbon species coelute with sulfur-containing compounds, hydrocarbon quenching is likely to occur. Self-quenching can also occur with high concentrations of heteroatoms (O, N, S). This effect stems from collisional energy absorption, competing chemical reactions, or reabsorption of photons by other species. Like many other techniques, improper gas flows rates and composition can result in severe degradation of the detector response. Detector response for sulfur-containing species decreases with temperature higher temperature or lower?. Detector response increases for phosphorus-containing species as temperature increases. Condensation and detector corrosion are viable concerns with the large influx of halogenated solvents.

FPDs have found specific uses in the chemical industry for the analysis of volatile sulfur-containing compounds, including H₂S, COS, CH₂SH and CS₂. FPDs are also used in the petroleum industry. Detection with FPD versus FID is shown below in Figure 9. The vast simplification of the FPD chromatogram versus the FID chromatogram demonstrates the highly selective nature of this technique.

B-16
Electrolytic Conductivity Detector. ELCD is a recently developed GC detector which is useful for the selective detection of halogenated compounds. Specifically, ELCDs are useful for detecting halogens, sulfur, or nitrogen-containing compounds. A GC effluent is mixed with a reaction gas which is either strongly oxidizing or reducing. The products from this reaction are joined with a deionized solvent to create an effective conducting solution which is directed into a conductivity detector. Its response is recorded as a signal. Those species which are ionized and lead to measurable changes in conductivity are selectively detected. This process of ionization can be controlled by the nature of the oxidizing/reducing agent introduced into the reaction chamber. Solvent flow rate, solvent purity, and general cleanliness affect the quality of the data.

Photoionization Detector. The PID uses light to create ions from the GC effluent. When photon energy in excess of a molecule's ionization energy is deposited in the molecule, photoionization occurs. The ionization energies of most organic molecules are in excess of 8 eV (Table 4). This energy corresponds to a photon wavelength of approximately 160 nm. This approach to effluent excitation, has two disadvantages: absorption of the photons by air molecules and incompatibility with fiber optic delivery. Photoionization by single photons is the basis for PIDs which are used in gas chromatography and organic vapor analyzers. Discharge lamps are the UV source. Anything with ionization energy less than that supplied by the lamp is detected. The specific light energy depends on the choice of gas and window material (e.g., metal fluoride). The most frequently used source is 10.2 eV which will ionize most molecules (the exception being the permanent gases, C₁–C₄ hydrocarbons, methanol, acetonitrile, and chloromethanes).²²
### TABLE 4

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ionization Potential, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>13.0</td>
</tr>
<tr>
<td>1,2 Dichloroethane</td>
<td>11.1</td>
</tr>
<tr>
<td>Methane</td>
<td>10.8</td>
</tr>
<tr>
<td>Hexane</td>
<td>10.2</td>
</tr>
<tr>
<td>Benzene</td>
<td>9.3</td>
</tr>
<tr>
<td>Toluene</td>
<td>8.8</td>
</tr>
</tbody>
</table>

PIDs are nondestructive, relatively inexpensive, of rugged construction, and easy to use. They have been shown to be 5 to 10 times more sensitive than FIDs for alkanes and approximately 50 times more sensitive for aromatic compounds. Because analyte detection is determined by the ionization potential of the specific analyte, and because chemical relationships exist between molecular structure and ionization potentials, detector response and chemical structure trends can be developed (Table 5).

### TABLE 5

<table>
<thead>
<tr>
<th>Relationship Between PID Response (10.2 eV) and Molecular Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity Increases as the Carbon Number Increases</td>
</tr>
<tr>
<td>Sensitivity for Alkanes &lt; Alkenes &lt; Aromatics</td>
</tr>
<tr>
<td>Sensitivity for Alkanes &lt; Alcohols &lt; Esters &lt; Aldehydes &lt; Ketones</td>
</tr>
<tr>
<td>Sensitivity for Cyclic Compounds &gt; Noneyclic Compounds</td>
</tr>
<tr>
<td>Sensitivity for Branched Compounds &gt; Nonbranched Compounds</td>
</tr>
<tr>
<td>Sensitivity for Fluorine Substituted &lt; Chlorine-Substituted &lt; Bromine-Substituted &lt; Iodine Substituted Compounds</td>
</tr>
<tr>
<td>Substituted Benzenes: Ring activators (electron-releasing groups) increase sensitivity. Ring deactivators (electron-withdrawing groups) decrease sensitivity (exception: halogenated benzenes).</td>
</tr>
</tbody>
</table>

**Spectral Detection.** Infrared absorption, mass spectral properties and atomic absorption and emission, have been used to detect and quantify the analytes of GC effluent. GC/MS and GC/FTIR are the most popular hyphenated techniques (combined instruments) in extensive use. Calibration curves must be prepared to quantify the analytes regardless of which detector is used. Low analyte recoveries at sample preparation stage must be taken into consideration when quantification is done using the calibration curves.

**FT-IR Detection.** IR absorption detection is a common method of analyte detection. As the GC effluents become separated and are near the end of their elution, the analytes enter into a sample cell.
commonly known as the light pipe. The light pipe is an integral part of a light generation and detection scheme which uses an IR-light source to characterize the distinct vibrational absorptions of each analyte. The wavelength and quantity of IR light absorbed by the analytes is dependent upon the number and type of functional groups present. Analyte identification is based in part on the nature of the functional groups inherent to each analyte.

IR source light passes through a beamsplitter. Of the resulting two beams, one is reflected off a stationary mirror and is directed back through the beamsplitter, through the light pipe, and into a detector. The other beam reflects off a moving mirror, is directed at the beamsplitter, and reflects through the light pipe and into the detector. The two beams impinging on the detector are out of phase, creating interference pattern. The pattern is analyzed using a Fourier transform algorithm, and the resulting values are recorded as an absorption spectrum.

Identification of an eluting species is made by comparison of an analyte’s IR spectrum with a set of spectra stored in computer memory. Analyte identification is based on elution time and spectral signature making the technique two-dimensional in nature. As a result, there is a high degree of certainty in the identification of analytes.

Mass Spectrometry Detection. MS has become a traditional method for analyte identification in nearly every modern analysis laboratory. MS offers the combined ability to be sensitive, selective, and applicable to a wide range of analytes. It has demonstrated a high degree of versatility and variation in its coupling to GC systems.

The basis of MS is the charged particle which, according to its mass and charge, follows different paths as it passes through magnetic and/or electric fields. Many analytes of interest are neutral species, and some means of ionizing them must be provided. MS is intrinsically a gas-phase technique, and electron impact is a common ionization method. The vaporized analyte in an effusive beam passes through a beam of electrons which cause loss of one or more electrons from the neutral analyte. The degree/efficiency of ionization depends on the kinetic energy (speed) of the electron beam. Ions are separated according to their mass/charge (m/z) ratio and are detected with an ion-sensing collector.

A primary concern in MS is the interface between the GC and the mass spectrometer. GC pressures are typically at atmospheric levels (760 torr), with flow rates in the range of 1–2 mL/min. Source pressures typically range from 2 to 10⁻⁵ torr for the two most common means of analyte ionization, namely chemical and electron impact ionization. Coupling open-tubed capillary columns to the ionization stage is often the simplest and quickest method for analyte preparation despite the pressure differential between components. Fused silica columns with immobilized separator phases offer low column-bleed properties and are highly inert, which is necessary for minimizing background signal. Although modern ionization methods can readily handle the 1–2-mL/min flow rates (usually helium), the pressure differential can affect the performance of the capillary column by varying the elution times of the analytes. Other methods of sample introduction include the use of a fixed inlet diverter or an open-split coupling. These methods reduce the amount of flow into the ionization source. Disadvantages generally involve the creation of undesirable dead volume (dead space) which creates loss in chromatographic resolution.
As previously mentioned, there are two primary methods of ionization: chemical and electron impact. Electron impact, the most commonly used method, involves a passing vapor stream which is impacted with high-energy electrons in the range of 5–100 eV (70 eV, typically), which knock off an electron from the gas-phase molecules. This process generally occurs in very low-pressure situations (10⁻³ torr) and is sufficient to maintain the analyte in the vapor phase. A softer source of ionization is sometimes necessary to prevent molecular rearrangement and, hence, loss of original molecular identity. Chemical ionization involves reactions between analyte molecules with a relatively high-pressure (0.2–2 torr) gas ion plasma. Collisional processes between the analyte and the gaseous constituents produce stable molecular ions which result in minimal rearrangements. This method, although useful, can produce a large degree of negatively charged species which are not detectable with traditional MS instrumentation.

There are several methods available for ion separation, all of which are based on the mass-to-charge ratio of the molecular ion. Ion separation and selection can be implemented using a magnetic sector apparatus, a quadrupole filter, or an ion trap device. Methods including time-of-flight or ion cyclotron resonance are generally not used in conjunction with GC. Briefly, a magnetic sector apparatus, an ion trap device, and a quadrupole filter all depend on the m/z ratio to deflect, to store and record ion motion, and to focus an ion, respectively. The magnetic sector and the quadrupole methods serve as means to transport the ions of interest to the detector. The electron multiplier is a common detector type. A Faraday cage collector is less commonly used. These methods produce a current resulting from the impingement of the ions on an electrode.

MS applications are varied and are readily applicable to nearly all volatile and semivolatile organic compounds. The primary constraint is that the analytes must form into the vapor phase and be capable of ionization via electron impact or chemical methods. By the nature of its vast abilities, MS has been difficult to operate and maintain. Down times in which the instrument is in repair or under normal maintenance are often frequent. Under these conditions, the cost on a per sample basis may restrict its use to applications in which specific analyte types and quantities are required. However, recent tabletop designs are proving to be more simple and more reliable.

**Atomic Emission Detection (AED).** AED identifies analytes according to spectral signatures inherent to their atomic structure. During the flow of column effluent, a reagent gas is added to the analyte stream. Upon reaching a reaction cavity, a microwave-assisted plasma discharge breaks down the analytes into their atomic constituents, many of which are electronically excited. Since the wavelengths of the photons emitted by the electronically excited atoms are well defined and fall within a set of narrow values, atomic emission (AE) serves as a very powerful method for elemental and, hence, analyte identification. The emitted photons are focused onto an optical grating, and the dispersed light is collected with a light-sensitive detector. Filters or distinct regions of the dispersed light are employed for monitoring selective element emissions. Figure 10 depicts several chromatograms recorded from a mixture of 23 EPA-considered water purgeables. The four chromatograms depict the Br, Cl, C, and H channels monitored with AED.

GC detection can be wide-ranging in its method of operation and the types of analyte species that can be detected. Usually, an analytical method is chosen for its ability to provide the operator with a specific piece of information such as molecular structure, need for sensitivity (trace analysis), or elemental, ionization, or conductivity differentiation. As shown in Figure 4, the most sensitive
Figure 10. Chromatograms of a solution of 23 water purgeables using atomic emission detector (AED). Each chromatogram uses a selective wavelength of the respective atomic species.

detectors for trace analysis include ECDs, NPDs, and mass spectrometers, while MS and FT-IR offer the greatest measure of analyte structure. The selective detectors include NPDs, FPDs, and ECDs. Specific applications for GC detectors are shown in Table 6. FIDs and mass spectrometers are nonselective detectors and are not included in the table below.

TABLE 6

<table>
<thead>
<tr>
<th>Analyte Type</th>
<th>Detector</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed Gases</td>
<td>TCDs, PIDs</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>FIDs, PIDs</td>
</tr>
<tr>
<td>Halogen Compounds</td>
<td>ECDs, ELCDs</td>
</tr>
<tr>
<td>Nitrogen Compounds</td>
<td>NPDs, ELCDs</td>
</tr>
<tr>
<td>Sulfur Compounds</td>
<td>FPDs, ELCDs</td>
</tr>
<tr>
<td>Phosphorus Compounds</td>
<td>FPDs, NPDs</td>
</tr>
<tr>
<td>Oxygen Compounds</td>
<td>FT-IR</td>
</tr>
<tr>
<td>Isomers</td>
<td>FT-IR</td>
</tr>
</tbody>
</table>
Problems with GC

Erroneous Identification of Peaks. In its usual form, the identification of analytes is based strictly on retention time. Usually an elution time window for a particular analyte is determined from standardization and calibration experiments. Peaks within that window are assigned to that analyte. Figure 11 shows a chromatogram of a gasoline mixture consisting of many organic compounds. Peak widths are a few minutes. Several of the peaks in the carbon channel are overlapped to such an extent that they are indistinguishable. Without an additional level of detector specificity, their separate contributions cannot be reliably determined.

If retention time changes by as little as 1%, the peak will fall outside the predetermined identification window. Changes in temperature, carrier gas purity, or flow rate can have a substantial effect on the retention times. These instabilities in retention times can cause false positive or negative assignments.

Baseline Correction Problems. Analyte features of interest are determined against background signal. This is especially true for trace analysis with complex environmental samples. Ultimately, it is the background signal magnitude and variability that determine the limit of detection. Any electronic noise in the chromatogram can lead to widely erroneous baselines. Because quantitation is determined via peak heights or peak areas, the background contribution must be adequately separated from that of the analyte (baseline correction).

Figure 11. AED of a MTBE and aliphatic alcohol-laced gasoline sample monitoring a) the carbon component and b) the oxygen component of the separated analytes. Note the heavily overlapped spectra in Part a.
Correct evaluation of the baseline for quantitation relies on the precision (level of statistical error) and accuracy (level of systematic error) which can be achieved. Precision is characterized by the repeatability or reproducibility of peak areas. A high level of repeatability refers to actual repetition of analysis of the same sample with the same technology and techniques, with the same results. A high level of reproducibility refers to analysis of the same sample using different technology, techniques, and operators, resulting in the same quality data.26

Test and calibration measurements must be executed to characterize precision and accuracy. Deviations from true values can then be detected and investigated as to their cause. The lack of pure substances for calibration measurements can be a major problem.

**Purging.** Purging (sparging) efficiency is never 100%, meaning, purging never transfers 100% of the analyte to the trap. In general, it is more important that the purging be reproducible than efficient. If the same amount of analyte is transferred in repeated purging with the same experimental protocol, it is considered reproducible. It is generally acceptable if only 10% of the analyte is transferred to the trap during a 10-minute purge. Purging efficiency can be affected by the temperature of the purge vessel. Higher temperature increases the volatility of gaseous species, increasing flow rates. Greater sparge gas flow rates generally result in increased mass transfer of the analyte to the analyte trap. The presence of other analytes can affect the sparging.

Laboratory standards do not always serve as reliable means for analyte quantification or calibration. For example, efficiency of sparging benzene from a water solution will not mirror the efficiency of sparging benzene from a solution with a high concentration of dissolved organic matter (or a different solvent). In a solvent other than water, if benzene is highly soluble, that solvent preferentially retains the benzene in solution. In other words, the sample matrix influences purging efficiency.

Ideally, standard solutions would be prepared from a matrix containing everything except the analyte of interest. However, this is often impossible owing to the singularity of environmental samples and their high degree of heterogeneity. For example, the addition of standard solution to soil matrices often requires lengthy periods of time (days to months) to reach a fully equilibrated state.

Standard additions involve the addition of small amounts of a standard solution or an analyte to a sample (see Section 4.2, Calibration Curves).

Standard additions may introduce bias into the procedure through loss of sample by preparation and testing procedures. This is overcome by using the sample matrix as the diluent. In either case, actual sample amounts are usually quite insignificant so that dilution effects become negligible.

**HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY**

The mobile phase of HPLC is liquid. The classical implementation uses gravity flow of the mobile phase through a relatively large-diameter packed column. However, modern HPLC implementation uses high-pressure pumps to force the mobile phase through small columns. HPLC usually operates at ambient temperatures and is especially appropriate for the analysis of nonvolatile substances.
and polar organic analytes that are not amenable to analysis by GC. A typical HPLC system consists of one or more solvent reservoirs, a pump, a sample injection system, one or several columns, the detector, and a data acquisition system (Figure 2).

Generally speaking, analytes tending to be polar (hydrophilic) and nonvolatile are analyzed with HPLC, while analytes which are nonpolar (hydrophobic) and volatile are best analyzed by GC separation. There are analytes which can be analyzed with either method depending upon the type of sample and the means of preparation.

A discussion regarding environmentally relevant analytes follows. Taking the natural course of sample analysis, it is important to note how each step in the process can influence the final analytical results.

Sample Preparation

There are several steps inherent to the preparation and injection of samples for HPLC. First, samples must be properly collected and stored. Secondly, removal of gross particulate matter and cleanup are necessary. Specifically, extraction and concentration steps are performed at this level. Sample preparation often includes fractionation of the sample by passing the analyte through guard columns, by performing multidimensional LC, or through chemical derivatization schemes.

Derivatization improves detectability of trace species and can be automated and integrated onboard within the analysis. This procedure is required if analytes cannot be detected because of the lack of chromophores. Derivatization is accomplished through the addition of UV-visible chromophores or a fluorescent tag.

Automation techniques such as those found in fractionization and derivatization steps provide a more economical means of preparation while improving time and sustaining method reliability. Specifically, the automation of HPLC valves, precolumn derivatization, solid-phase extraction, and SFE devices has helped to control environmental analysis costs.

Four of the most common extraction methods for environmental samples are Soxhlet extraction (liquid-solid), SFE, LLE, and SPE. The most traditional of these methods are the Soxhlet and the LLE methods.

* Liquid–Liquid Extraction (solvent extraction). In this method, the sample containing the analyte is a liquid solution, typically a water solution, that also contains other solutes. Separation is necessary when the original solvent or other solutes interfere with the chosen analysis technique. Extraction takes place in a separatory funnel. Both sample and solvent (two immiscible liquids) are placed in the funnel which is tightly stoppered. It is then shaken and vented, this process being repeated until the extraction is quantitative. At initial contact, the solute moves from the original solvent to the extracting solvent and then back to the original solvent. An equilibrium is reached when the rates of movement are equal. The amount of analyte that gets extracted depends on the relative distribution between the two layers, which, in turn, depends on the solubilities of the two layers.
**Soxhlet Extraction.** A Soxhlet extraction is the process by which a constant flow of pure solvent from a condenser is allowed to saturate a sample. After saturation the solvent and dissolved analytes are collected at the bottom of the distillation apparatus where further solvent vapor is produced for condensation above the sample. As with SFE, or ultrasonic liquid extraction, the solid sample must be homogenized before placement into the Soxhlet apparatus. The Soxhlet method has well-defined procedures for selective sample extraction with a wide range of selective solvents.

**Supercritical Fluid Extraction.** One of the methods which has received widespread attention for analyte extraction from solids involves the application of supercritical fluids. The extraction media are usually gases at ambient conditions which are vented (e.g., CO₂, which is nontoxic and inexpensive). The solvent strength of the CO₂ supercritical fluid can be varied by manipulating temperature and pressure. SFE is also amenable to chemical modifiers, (e.g., methanol), which optimize solubility by affecting polarity and competition among sorptive sites on the sample matrix.

SFE involves two modes. In the static mode, the matrix sample is placed within an extraction chamber and an equilibrium state is created in which the supercritical fluid extracts the volatiles from the sample. In the dynamic mode, a constant stream of fresh supercritical fluid is flushed through the sample chamber and the volatiles are carried away to the chromatograph. On-line extractions, in which the analytes are flushed directly into the chromatograph, or off-line extractions, in which the analytes are recovered and then injected into the chromatograph can both be used with SFE.

**Solid Phase Extraction.** (SPE) is another way to clean up water samples before injection onto the analytical column. Compounds or classes of compounds of interest are selectively adsorbed onto solids and then later eluted. Such eluted samples are generally more concentrated (preconcentrated) than the original sample and result in the additional advantage of lowering the detection limit. This type of sample enrichment can be done at the site itself, thereby lowering transport costs and eliminating problems arising from sample instability. This form of extraction is becoming increasingly popular within analytical chemistry laboratories.

**Sample Injection**

Placement of the analyte mixture into older, lower-pressure HPLC chromatographs involves injection of the sample directly through the septum. This, however, runs the risk of material being dissolved from the septum into the flow stream. Loop valves are now traditionally used to introduce samples into the mobile phase. The valve rotates into one position at a precisely known volume, for example, 10 µL, fills with sample, rotates again, and introduces the sample into the main solvent stream for separation. Loop valves are available from many manufacturers in both manual and computer-controlled versions suitable for automatic sampling. Manual injectors are advantageous as they are inexpensive and easy to operate. However, manual injectors do not have a high degree of reproducibility and cannot be coupled with on-line derivatization equipment. The injecting syringe must be taken off-line and manually cleaned.

Automatic equipment is available for injection and pretreatment and most are capable of handling 0.1 to 100 µL of analyte sample per given injection. Pretreatment capabilities include in-line programmable systems which can heat, cool, dilute, add small amounts of internal standard, or
derivatize a given sample. Although these options add a high degree of precision to the analysis, they are costly and require a high level of operational training.

Elution of analytes from the column with a solvent of constant composition is known as isocratic elution. More versatile chromatographic methods are possible with gradient elution, in which the composition of the mobile phase is controlled. Most forms of gradient elution employ separate reservoirs and pumps for individual solvents, which are then mixed in a predetermined sequence of volume ratios. Binary mixing is standard, but ternary (three solvent) and quaternary programmers are available. The versatility of gradient elution arises from the ability to optimize the separation of mixtures with substantially different retention characteristics. The solvent composition-time profiles may be linear, logarithmic, parabolic, etc. Temperature programming is not a common feature of liquid chromatography, although column heaters for stabilization of retention times are available.

The ideal HPLC pump has a pulse-free flow, a high-precision flow rate, a working flow rate range, and the ability to maximize the flow rate. Also important is a low dead volume and the ability to handle more than one mobile phase for gradient conditions. Conventional flow rates for HPLC units range from 0.3 to 10 mL/min. Narrow bore columns generally have flow rates from 0.05 to 5 mL/min. Pumps are important since they affect the performance of the flow rate and the composition of the mobile phase. Thus the shape and elution of the peaks and the overall quality of the data can be directly traceable to this one instrumental component. The choice of a pump design is mandated by whether an isocratic or gradient elution is employed and whether narrow-bore or standard-bore columns are used.

Solvent degassing is essential in HPLC. Dissolved gases in the mobile phase may cavitate the pump. Gas or air bubbles can lead to column voids which ultimately damage the column and lead to loss of resolution. Degassing of aqueous elements can be implemented via bubbling helium through the mobile-phase reservoir. Another option includes the use of a membranous polymer matrix formed into a tube. The polymer is permeable to gas, but not the liquid phase. The application of a vacuum outside the tube results in dissolved gases permeating through the tube and out of the mobile phase. This method suffers from increased deadspace (undesirable space that leads to band broadening) and has the potential for bleed of the polymer matrix into the chromatographic flow.

**Columns**

Columns. HPLC has many variations which are identified by mode of separation. Adsorption of analytes on polar solids (column-packing material) followed by elution with a liquid–phase is termed liquid–solid (adsorption) chromatography. Many HPLC adsorption stationary phases are named according to the types of stationary materials employed. These materials can be regular, irregular, or pellicular in shape. They have a solid core (30-μm diameter), usually a glass bead, which is used to support a porous material consisting of silica or alumina (2–3 μm thick). The glass serves as a rigid core for high-pressure applications in which the softer porous layer serves as the stationary phase for analyte separation. There are two variations of this technique. In normal-phase chromatography (NPC), the analytes are adsorbed onto a polar material, alumina, or silica gel in a relatively nonpolar solvent. The mobile phase can consist of hexane, cyclohexane, chloroform, carbon tetrachloride, benzene, and toluene. Because of the ionic and hydrogen bonding, the analytes are polar in nature and
are eluted by liquids of higher polarity in the isocratic or gradient mode. The alumina and silica gel may be used unmodified.

Recently, bonded silica (silica surface chemically bonded to various organic groups) has been used. The stationary phase acts as a liquid bonded to the solid alumina support. This is actually LLC. Different selectivities are provided based on partitioning originating from the hydrogen bonds and hydrophobicity (also termed, bonded-phase chromatography). The stationary material usually is composed of Si–O bonding sites that are bonded with a variety of alkyl constituents which include polar functional groups such as −CN (cyano), −NH₂ (amine), or CHO–CH₂OH. These functional groups are reflected in the manufacturer’s names for their products. Examples include Chromegabond DIOL, LiChrosorb DIOL, MicroPak-CN, uBondapak-CN, Nucleosil-NH₂, and Zorbax-NH₂.

**Reverse-Phase Chromatography (RPC).** The column material is nonpolar and initial retention of the analytes is done in a relatively polar solvent. The analytes are nonpolar. Elution is carried out with polar or progressively polar mobile phase. These mobile phases include water, methanol, acetonitrile, and acetic acid buffered solutions. Silica columns bonded with C₈–C₁₈ carbon chains, trimethylsilane derivatives, phenyl derivatives, amino, diol, amide, sulfonic acid, carboxylic acid, and quaternary amine form the column-packing material (bonded-phase chromatography). Carbon chain columns are named according to the number of carbon atoms present. C₁₈ chains are typically referred to as octadecyl (ODS) type columns. Examples of column names include Partisil ODS-2, uBondapak-C₁₈, Spherisorb ODS, uBondapak Phenyl, Hyposil-SAS, and Nucleosil C-8.

**Column Selection.** Separation of a complex mixture will depend on the mechanism of the specific column, the nature of the mobile phase, and the components inherent to the mixture. A list of HPLC separation schemes and their general application to mixtures is outlined in Table 7. In practice, optimizing separation may prove to be systematic. Often it is necessary to experiment with various column types, different mobile phases, or mobile phases consisting of mixtures of various solvents. In general, the stationary phase should have a high affinity for the analytes, greater than the mobile-phase. Optimization of flow rate, mobile-phase ratio(s), temperature, gradient elution, and particle size are also required. The nature of the detector response will impact the degree of relevance of each parameter.

Protection of the analytical column is very important, especially in the application of HPLC to complex environmental samples. Filters which eliminate particulates and guard columns to trap strongly retained chemical species are simple and essential elements of HPLC. The analytical column can be easily clogged and rendered useless by larger particulates that are allowed to enter the flow stream. Guard columns, which are short sections of stationary phase, act as disposable filters for species that might be retained tenaciously on the analytical column.

**Size Exclusion Chromatography (SEC).** SEC is also known as gel permeation chromatography (GPC). The separation is based on molecular size. The column is composed of a porous gel that allows preferential entry of small molecules, resulting in the elution of larger analytes.
**TABLE 7**

<table>
<thead>
<tr>
<th>Chromatographic Method</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal and Reverse-Phase</td>
<td>Low formula weight (&lt;200 amu)</td>
</tr>
<tr>
<td></td>
<td>Nonionic</td>
</tr>
<tr>
<td></td>
<td>Polar or nonpolar</td>
</tr>
<tr>
<td></td>
<td>Water or organic soluble</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Low to moderate formula weight (&lt;2000)</td>
</tr>
<tr>
<td></td>
<td>Nonpolar</td>
</tr>
<tr>
<td></td>
<td>Organic soluble</td>
</tr>
<tr>
<td>Ion-Exchange</td>
<td>Low to moderate formula weight (&lt;2000)</td>
</tr>
<tr>
<td></td>
<td>Ionic</td>
</tr>
<tr>
<td>Size-Exclusion</td>
<td>Low to high formula weight</td>
</tr>
<tr>
<td></td>
<td>Nonionic</td>
</tr>
<tr>
<td></td>
<td>Water or organic soluble</td>
</tr>
</tbody>
</table>

*Ion-Exchange Chromatography (IC).* IC uses an ion-exchange resin as column packing. In general, smaller particle sizes (in the order of micrometers) of the packing material produce better separation efficiencies. Higher pressures and longer column lengths also contribute to better separations.

**Detectors**

*Detectors.* There are a number of options for detection of analytes as they elute from the column. Light-based detectors (absorbance, fluorescence, and refractive index) are the most widely used because they are well adapted to handling large excesses of solvent. Thermospray options that quickly volatize the solvent are available for HPLC, but are not widely used as a practical method. The operations of absorbance and fluorescence detectors are discussed in Section 6.

Absorbance detectors require that the analyte have a suitable chromophore (light-absorbing functional group). Alkanes and simple alkenes absorb light at wavelengths shorter than the solvent cutoff so they cannot be detected by either conventional absorbance or fluorescence. Most other organic compounds absorb in the ultraviolet and are suitable for absorbance detection. The absorbing power of molecules can vary from one wavelength to another, so the capability of changing the wavelength is important.

Absorbance detectors can be single, fixed-wavelength, multiple discrete wavelengths, or they can acquire the entire absorbance spectrum with a photodiode array. Table 8 shows recommended
wavelengths for various classes of organic compounds. Absorbance detectors are used heavily for analysis of drugs, pharmaceuticals, metabolites, and PAHs.

### TABLE 8

Absorption Wavelengths of Common Chromophores

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>Example</th>
<th>Solvent</th>
<th>(\lambda_{\text{max}}) nm</th>
<th>(\varepsilon_{\text{max}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkene</td>
<td>(\text{C}<em>6\text{H}</em>{13}\text{CH}=\text{CH}_2)</td>
<td>(n)-Heptane</td>
<td>177</td>
<td>13,000</td>
</tr>
<tr>
<td>Alkyne</td>
<td>(\text{C}<em>7\text{H}</em>{11}\text{C}=\text{C}--\text{CH}_3)</td>
<td>(n)-Heptane</td>
<td>178</td>
<td>10,000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>196</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>225</td>
<td>160</td>
</tr>
<tr>
<td>Carbonyl</td>
<td>(\text{CH}_3\text{COCH}_3)</td>
<td>(n)-Hexane</td>
<td>186</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>(\text{CH}_3\text{COH})</td>
<td>(n)-Hexane</td>
<td>280</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>180</td>
<td>large</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>293</td>
<td>12</td>
</tr>
<tr>
<td>Carboxyl</td>
<td>(\text{CH}_3\text{COOH})</td>
<td>Ethanol</td>
<td>204</td>
<td>41</td>
</tr>
<tr>
<td>Amido</td>
<td>(\text{CH}_3\text{CONH}_2)</td>
<td>Water</td>
<td>214</td>
<td>60</td>
</tr>
<tr>
<td>Azo</td>
<td>(\text{CH}_3\text{N}=\text{NCH}_3)</td>
<td>Ethanol</td>
<td>339</td>
<td>5</td>
</tr>
<tr>
<td>Nitro</td>
<td>(\text{CH}_3\text{NO}_2)</td>
<td>Isooctane</td>
<td>280</td>
<td>22</td>
</tr>
<tr>
<td>Nitroso</td>
<td>(\text{C}_4\text{H}_7\text{NO})</td>
<td>Ethyl ether</td>
<td>300</td>
<td>100</td>
</tr>
<tr>
<td>Nitrate</td>
<td>(\text{C}_4\text{H}_3\text{ONO}_2)</td>
<td>Dioxane</td>
<td>665</td>
<td>20</td>
</tr>
</tbody>
</table>

\(\lambda\) = wavelength.

\(\varepsilon\) = absorptivity.

**Fluorescence Detectors.** Like absorbance, fluorescence is usually initiated with a single fixed excitation wavelength. Fluorescence emission can be monitored at a single fixed wavelength or can be well defined by acquiring an emission spectrum. Fluorescence detectors are especially important for PAH analysis.

Both spectrophotometric and fluorimetric detection can be enhanced by postcolumn derivatization to analytes which do not intrinsically possess the requisite spectroscopic characteristics. The reagents chosen for tagging should have an absorption maximum which not only improves sensitivity, but which increases selectivity. Table 9 lists several UV-visible chromophores and fluorescent tags which assist in HPLC analysis and optimal wavelengths for spectroscopic detection.

Additional examples include the formation of dansyl derivatives for detection of amino acids. Cerate oxidimetry is a derivatization technique which is based on the reduction of Ce(IV) by other compounds. Ce(II) produced in the reduction step is measured by fluorimetry. Dithiocarbamate derivatives (for bismuth, cadmium, copper, mercury, iron, nickel), zincon complex (postderivatization for zinc), dithiozine derivatives (for bismuth, cobalt, copper, manganese, mercury, nickel, lead) have been used, along with many other metallic element derivatives. Detection limits in the parts-per-million range are very common. Analyte derivatization can be performed either precolumn (on-line or off-line) or postcolumn. Postcolumn derivatization is almost always performed on-line and requires
TABLE 9

UV-Visible Functional Groups and Fluorescent Tags for HPLC Analysis

<table>
<thead>
<tr>
<th>Target Functionality</th>
<th>Structure</th>
<th>Reagent</th>
<th>λ₁, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorbance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alcohols</td>
<td>-OH</td>
<td>Phenylisocyanate</td>
<td>250</td>
</tr>
<tr>
<td>Oxidizable Sulfur</td>
<td>SO₂⁻²</td>
<td>2,2'-Dithiobis (5-nitro-pyridine)</td>
<td>320</td>
</tr>
<tr>
<td>Fatty Acids</td>
<td>-COOH</td>
<td>p-Bromophenacyl bromide</td>
<td>258</td>
</tr>
<tr>
<td></td>
<td>=C=O</td>
<td>2-Naphthacil bromide</td>
<td>250</td>
</tr>
<tr>
<td>Aldehydes and Ketones</td>
<td>-CO-</td>
<td>2,4-Dinitrophenyl-hydrazine</td>
<td>365</td>
</tr>
<tr>
<td></td>
<td>COOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>=C=O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary Amines</td>
<td>-NH₂</td>
<td>o-Phthalaldehydes (OPA)</td>
<td>340</td>
</tr>
<tr>
<td>Primary and Secondary</td>
<td>-NHR</td>
<td>9-Fluorenylmethylchloroform (FMOC)</td>
<td>256</td>
</tr>
<tr>
<td>Amines</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorescence</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alcohols</td>
<td>-OH</td>
<td>Phenylisocyanate</td>
<td>230 exc</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>315 em</td>
</tr>
<tr>
<td>Primary Amines</td>
<td>-NH₂</td>
<td>o-Phthalaldehydes (OPA)</td>
<td>230 exc</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>455 em</td>
</tr>
<tr>
<td>Primary and Secondary</td>
<td>-NHR</td>
<td>9-Fluorenylmethylchloroform (FMOC)</td>
<td>266 exc</td>
</tr>
<tr>
<td>Amines</td>
<td></td>
<td></td>
<td>315 em</td>
</tr>
</tbody>
</table>

λ = wavelength

the use of extra pumps, reaction chambers, and heating devices. These extra steps invariably introduce dead volume into the analysis and lead to loss of resolution. Postcolumn derivatization is costly because of the complexity of the apparatus and operator expertise required for proper analysis. Derivatization is compatible only with standard bore columns.

Refactrometry detectors measure changes in the refractive index (RI) of the effluent. The RI, the ratio of the speed of light in a vacuum to the speed of light in liquid, changes during the passage of the analyte plug and forms the basis of the technique. Refractometric detectors are universal, all substances having their own characteristic refractive index (any solute can be detected as long as there is a difference in RI between the solute and the mobile phase). However, RI detectors are not very sensitive, and output is subject to temperature changes and composition of the mobile phase. RI detectors are generally unsuitable for gradient elution work because of their sensitivity to mobile-phase composition.²⁴,²⁵

Electrochemical detectors measure current associated with the oxidation or reduction of solutes. Amperometric, the most commonly used detectors, oxidize or reduce only small quantities of solute (<1%). Currents are observed as nanoamps and are not difficult to measure. Amperometric detectors have a high sensitivity. Coulometric detectors employ a multielectrode with up to four graphite electrodes. It produces better signal-to-noise ratio than the amperometric detectors, and its porous electrodes are less susceptible to surface degradation. A sensing/working electrode is
maintained at a constant potential, while the current is measured as the eluent carrying redox species moves over the electrode. Electrochemical detection systems require conducting mobile phases. The nature of electroanalytical methods is discussed in more detail in Section 8.

FT-IR, MS, atomic absorption (AA), and plasma emission have been employed as detectors. The large volumes of solvent in HPLC compared to the amount of the analyte makes the removal of the analyte problematic in MS. Plasma emission, FT-IR, and flame AA detectors can be used on-line with less difficulty. Section 6 will discuss the nature of spectroscopic methods.

The precision for HPLC experiments generally lies in the 1%–10% range. The selectivity in HPLC, as in any other chromatographic technique, is determined by a combination of the column and detector characteristics. The column alone may account for 1%–4% of the uncertainty. Limits of detection depend on the particular detector. Analytes passing through the detector region can be diluted, lost, or structurally modified. Thus, efficiency of separation and the particular mode of detection can affect sensitivity. Some characteristics of HPLC detectors are shown in Table 10.

The applicability of HPLC techniques in the fields of organic chemistry and biological chemistry is very broad. HPLC covers many classes of compounds, including PAHs, phenols, acids, aliphatic hydrocarbons, ketones, aldehydes, esters, herbicides, and pesticides.

### TABLE 10

<table>
<thead>
<tr>
<th>Detector</th>
<th>Sensitivity/Selectivity</th>
<th>Advantages</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV Variable $\lambda$</td>
<td>Medium/low</td>
<td>Low-cost universal</td>
<td>Aldehydes and sulfate after derivatization</td>
</tr>
<tr>
<td>UV- Diode Array</td>
<td>Medium/medium</td>
<td>Selectivity</td>
<td>Pesticides, PAHs, phenol, surfactants, nitroaromatics, inorganics</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>High/medium</td>
<td>Sensitivity</td>
<td>PAHs, carbamates, glyphosate</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>Low/low</td>
<td>Universal</td>
<td>Universal</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>High/medium</td>
<td>Sensitivity</td>
<td>Phenols, amines</td>
</tr>
<tr>
<td>Mass Spectrometer Scan</td>
<td>Low/medium</td>
<td>Structure</td>
<td>Pesticides, PAHs</td>
</tr>
<tr>
<td>Mass Spectrometer SIM</td>
<td>Medium/high</td>
<td>High selectivity</td>
<td>Pesticides, nitroaromatics</td>
</tr>
</tbody>
</table>

**HPLC: Its Application to PAHs**

PAHs represent a diverse class of environmentally important wastes that result from incomplete combustion processes. PAHs are a constituent of fossil fuels and are found near ruptured
fuel storage tanks, fuel dumps, spill sites, and creosote and coal tar lining locations. PAH contamination of groundwater represents a serious environmental threat. Cleanup activities are required and are highly regulated.

PAHs can be extracted from solid, liquid, and gaseous phases. Soil extractions can be undertaken using Soxhlet, sonification, or SFE. SPE or LLE is quite simple for contaminated water samples. Absorption methods are generally used for contaminated air samples. Below is a list of officially used extraction techniques for the determination of PAHs in a variety of matrices:

- EPA 550.0 for drinking water with LPE
- EPA 550.1 for drinking water with SPE
- EPA 610 for wastewater
- EPA 8310 for water and solid waste
- EPA IP-7 for indoor air
- EPA TO-13 for ambient air
- German DIN 38407 F8 for drinking water
- German VDI (3875) for ambient air
- French NF-X43-025 for ambient air

HPLC has found a special niche application in the determination and quantification of PAHs. Typically chromatographic conditions consist of using reverse phase, normal bore analytical columns at constant temperature. Isocratic elutions (using a single solvent for the mobile phase) and gradient elutions are equally common. Fluorescence detection is the method of choice and can be undertaken using either a single photomultiplier tube (PMT) or a diode-array detection scheme which measures the spectral response. PMT detection offers a high degree of sensitivity for low-concentration contaminants, although spectral information (and selectivity) is lost. The detection limits for PAHs range from 0.3–40 pg for fluorescence at single-wavelength fluorescence detection. Diode-array detection limits range from 50 to 500 pg. The corresponding linear dynamic ranges are 0.01–1 ng and 0.1–10 ng.

**OTHER CHROMATOGRAPHIES**

**Ion-Exchange Chromatography**

In IC, the stationary phase is anion-exchange resin, and separation depends on the intensity of interactions between ionic solutes and exchange sites on the resin. Sample volumes of a 10–500 μL are introduced by manual syringe injection or automatic/manual injection loops, while electrolyte solutions are used as the eluting mobile phase. Ions in the sample mixture partition between the charged ionic functional groups on the resin surface and an appropriate counter-ion (opposite charged ion) in the mobile phase. Table 1 lists ion-exchange stationary phases and their corresponding functional charge types.
TABLE 11

<table>
<thead>
<tr>
<th>Manufacturer Name</th>
<th>Functional Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion-X-SC</td>
<td>Cation</td>
</tr>
<tr>
<td>Partsil 10 SCX</td>
<td>Cation</td>
</tr>
<tr>
<td>Amberlite IR-120</td>
<td>Cation</td>
</tr>
<tr>
<td>Dowex 50W</td>
<td>Cation</td>
</tr>
<tr>
<td>Ion-X-SA</td>
<td>Anion</td>
</tr>
<tr>
<td>Partsil 10 SAX</td>
<td>Anion</td>
</tr>
<tr>
<td>Amberlite IRA-400</td>
<td>Anion</td>
</tr>
<tr>
<td>Dowex 1</td>
<td>Anion</td>
</tr>
</tbody>
</table>

The separation of ions results from differential ion-exchange rates within the column resin. In general, organic cations elute from the column faster than inorganic cations. This is attributed to the relatively large size of organic anions which have an effectively weaker binding to the ionic stationary phase.

The predominant detection scheme in IC is conductivity. Eluents must be chosen accordingly. Conductivity detection is practiced in two modes, suppressed (SCIC [suppressed conductivity ion chromatography]) and nonsuppressed. If the eluents have sufficiently low conductivity, conventional (nonsuppressed) IC can be carried out without a suppressor column. However, the high conductivity of the strong electrolytes in the eluting solution can easily swamp the conductivity changes associated with the analytes. The function of the suppressor column, inserted between the analytical column and the conductivity detector, is to neutralize the strong electrolytes, particularly hydrogen and hydroxyl ions. The suppressor column acts as an ion exchanger.

The mechanism of suppression initially involves an exchange of ion from the eluent to the column. For example, exchanging a chloride ion with a hydroxyl from the strong electrolyte, hydrochloric acid, acts as ionic suppression. The hydroxyl will be consumed by the hydrogen ions to form neutral water molecules. In the process, the chloride ion of the eluent is removed from the solution. Suppressor columns periodically require regeneration.

Extremely dilute solutions can be preconcentrated by passing them over adsorbing resins. The IC column is made of derivatized polymeric materials which are of small particle size, about 20 femtomole (fm). Cation-exchange resins like sulfonated polystyrene-divinyl benzene, and anion-exchange resins like quaternary amine functionalized styrene divinyl benzene, silica, or polyacrylates are widely used. The columns are relatively short, approximately 24–40 cm in length, with a 10-mm ID.

Various electrolytes have been used as mobile-phase eluents, including alkali metal hydroxides, dilute acids, salts (pyridinium, silver, cupric for cations), and salt mixtures (carbonate and bicarbonate, borate and gluconate, phthalate for anions). Often a single column is used to separate
ions (cations/anions), whereby the selectivity is achieved by the choice of the eluent. This is an inexpensive approach to utilizing many columns to do an analysis. Furthermore, IC is amenable to both isocratic and gradient elutions. The isocratic mode is time-consuming for multiple ions. Gradient elution employs a technique called isocratic elution in which two mobile-phase components with the same conductivity are used. Using isoconductive gradients, weak and strong electrolytes are balanced, while the elution strength is changed during the analysis. This technique inhibits baseline shifts, yields fast equilibration times, and improves peak shapes and sensitivity of later eluting analytes. Fewer instrumental components, lower costs, and less maintenance are additional advantages.

A disadvantage of IC is the limited selectivity of the columns which often results in coelution of analytes. In such cases, two columns in parallel configuration with a column-switching valve (coupled IC) can be employed. By switching between the two columns, two analyses can be performed with a single injection. Both columns need not be ion-exchange columns; ion-exclusion columns may also be used.

IC is widely used for quantitative inorganic ion analysis. Similar to the other chromatographic techniques, quantitative analysis requires calibration curves. The dynamic range of detection in the suppressed mode is four times greater than the unsuppressed mode range. Suppressed mode is superior in the detection limits as well, which range from the parts-per-billion (μg/L) level to the parts-per-million (mg/L) level (Table 12). Precision, as indicated by the relative standard deviation, lies in the 1%-4% range. All ions (inorganic) encountered in environmental situations can usually be analyzed with good selectivity.

Preconcentration and larger injection volumes yield lower LODs. In addition to those listed, other simple ions analyzed by IC include chlorate, chlorite, hydrogen phosphate, chromate, arsenate, selenite, acetate, cyanide, formate, bromate, citrate, oxalate, fumarate, various amino acid ions, and metal ions such as lithium, zinc, barium, and lanthanum. Pollutants such as phenoxy acid herbicides can be analyzed by IC with either UV or conductivity detection, but are routinely done by GC after derivatization.

Polymeric columns have been constructed with both reverse-phase properties and ion-exchange properties in the same resin to separate difficult analyte mixtures. Nonmetallic gradient pumps must be employed since changes in solvent, acidity, and ionic strength all occur during a run. These columns have successfully separated nitrogen-containing aromatics, sulfonated organics, and organic dyes. As with any other chromatographic technique, there are a variety of factors which influence retention in ion-exchange chromatography. Table 13 below lists these factors and their influence upon the retention process.

A variation of IC known as chelation IC demonstrates transition metal and lanthanide detection at the parts-per-billion (μg/L) level. Chelation is the multiple binding of a molecular moiety (particle) to a metal atom. It is often used as a preconcentration technique for transition metal ions. This process eliminates alkali and alkaline earths from the matrix, after which the filtered analyte mixture is subsequently introduced into the separation column by elution. When inductively coupled argon plasma spectrometers (ICAPs) are used to determine metal ions, elimination of alkali/alkaline earths...
### TABLE 12

<table>
<thead>
<tr>
<th>Analyte</th>
<th>LOD, μL</th>
<th>Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromide</td>
<td>4–100</td>
<td>Suppressed</td>
</tr>
<tr>
<td>Chloride</td>
<td>2–800</td>
<td></td>
</tr>
<tr>
<td>Fluoride</td>
<td>2–20</td>
<td></td>
</tr>
<tr>
<td>Nitrate</td>
<td>3–20</td>
<td></td>
</tr>
<tr>
<td>Nitrite</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Phosphate</td>
<td>0–700</td>
<td></td>
</tr>
<tr>
<td>Sulfate</td>
<td>4–300</td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td>240–500</td>
<td>Nonsuppressed</td>
</tr>
<tr>
<td>Nitrate</td>
<td>70–200</td>
<td></td>
</tr>
<tr>
<td>Sulfate</td>
<td>200–1240</td>
<td></td>
</tr>
<tr>
<td>Ammonium</td>
<td>4</td>
<td>Suppressed</td>
</tr>
<tr>
<td>Potassium</td>
<td>1–20</td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>400</td>
<td>Nonsuppressed</td>
</tr>
<tr>
<td>Magnesium</td>
<td>240</td>
<td></td>
</tr>
<tr>
<td>Potassium</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

minimizes spectral interferences to the ICP signals, especially at μg/L levels. Thus there are improvements in analytical detection limits and sensitivities. The standard deviation of the chelation IC method is in the 1%–10% range. The detection limits for cadmium, cobalt, copper, iron, nickel, manganese, and lead are 0.2–1 μg/L. Postderivatization of the ions to form colored compounds allows detection by UV–VIS spectrophotometry.

### Capillary Electrophoresis

The basic capillary electrophoresis (CE) technique is commonly referred to as capillary zone electrophoresis (CZE), but a number of variations exist. A popular version of CE is capillary ion analysis (CIA), which is used for the analysis of organic and inorganic ions. Other techniques include micellar electrokinetic capillary chromatography (MECC); capillary gel electrophoresis (CGE), commonly applied to biological species in which size-based separation of proteins and nucleic acids is required; capillary isoelectric focusing (CIEF); and capillary isotachophoresis (CITP).
TABLE 13

IC Parameters and Retention Properties

<table>
<thead>
<tr>
<th>Mobile-Phase Parameters</th>
<th>Change in Mobile-Phase Characteristics</th>
<th>Changes in Retention Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic Strength</td>
<td>Solvent Strength</td>
<td>Increases in ionic strength increase solvent strength. The primary effect on selectivity is relevant to whether or not different charged species are present in the analyte mixture. Properties of the mobile-phase counterion affect analyte-stationary phase interactions.</td>
</tr>
<tr>
<td>pH</td>
<td>Solvent Strength</td>
<td>Increases in pH result in increases in retention for anion exchange. There are corresponding decreases for cation exchange. Small changes in pH can have a substantial effect on analyte selectivity.</td>
</tr>
<tr>
<td>Temperature</td>
<td>Efficiency</td>
<td>Increases in temperature increase the interaction exchange rate of analytes between the mobile phase and the stationary phase. Higher temperatures lower the viscosity of the mobile phase.</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>Efficiency</td>
<td>Flow rates are generally lower than are found in comparable HPLC techniques. Lower rates result in better resolution and assist in the mass transfer kinetics.</td>
</tr>
<tr>
<td>Buffer Salt</td>
<td>Solvent Strength and Selectivity</td>
<td>Solvent strength and selectivity are impacted by changes in buffer and the type of counterion used. Changes in mobile-phase pH are also impacted by buffer changes.</td>
</tr>
</tbody>
</table>

Although not a standard analytical technique in the répertoire of commercial analytical laboratories, CE deserves special attention in that it is gaining widespread use and recognition as a sensitive and versatile technique for analyte detection and quantification. The characteristics of CE include using a narrow-bore (25–75-μm ID), fused silica capillary (25–75 cm long) instead of the larger-bore HPLC column for separation. CE operates by applying high voltages (10–30 kV) and high electric fields (100–500 V/cm) across the capillary. High separation efficiency, short analysis times, and the versatility of using several operational modes are only a few of the advantages of CE. CE can operate in an aqueous medium; it allows for simple methods development; and it can be fully automated.

CGE is the instrumental implementation of electrophoresis which involves the separation of ionic species dissolved in a gel matrix under an electrical gradient which drives the separation of the charged species. Ions are separated by their electrophoretic mobility through the porous gel network.
The separation space is within the confines of a capillary tube. The capillary is filled with a buffer solution and ionic analytes are introduced into the capillary tube as a plug at one end. The ionic analytes are then subjected to a very high electric field. CZE separates ions according to their relative mobility through a free solution. The mechanism of separation is the differential velocities of ionic species in electric fields. Positive ions (cations) move toward the cathode, while negative ions (anions) move toward the anode. The analytes leaving the capillary are detected by an on-line detector (UV/fluorimetric/laser-induced fluorescence/conductivity) to obtain the electropherogram. The ionic velocities depend on the ionic mobility within the capillary environment. Applications are designed to affect the analysis based upon the electrophoretic mobility alone.

Electroosmotic flow (EOF) is a fundamental principle underlying the operation of CE. At pH buffers equal to or greater than 7, the silanol groups of the inner surface of the capillary are deprotonized and become negatively charged. As a result, cations from the buffer solution move towards the interior capillary surface to counter the negative charges. This results in the formation of the Stern layer which is composed of a layer of negative silanol species covered by a positive layer of the parameters which can be fine-tuned during a CE experiment. Thus the buffer solution is contained within a sleeve of positive charge. Upon application of a high voltage, the buffer moves as a bulk towards the cathode. This movement carries with it all ionic and neutral analytes. If the electroosmotic velocity is higher than the electrophoretic velocity (velocities of individual ionic analytes within the electric field), one can observe the ions moving toward the electrode of the same charge. This effect is used to detect ionic and neutral species at a single detector. Under the electroosmotic effect, cations will be detected first and anions last if the detector is placed near the cathode. It should be noted that the electroosmotic effect can be completely eliminated by using additives in the buffer. The EOF process is depicted in Figure 12.

Figure 12. Process of electroosmotic flow development within the capillary: a) negatively charged fused silica surface (Si-O), b) hydrated cations accumulating near surface, and c) bulk flow towards the cathode upon application of electric field.
With the driving force of the flow uniformly distributed along the cross section of the capillary, the electroosmotic front maintains a flat flow profile rather than a parabolic shape indicative of laminar flow. This flat flow profile is depicted in Figure 13 and results in well-defined analyte peaks.

The presence of plug flow does not fully account for low zone broadening — the initial narrow zone of the total sample splits off into new zones depending on the number of separable species. Zone broadening results in lower efficiency. Elimination of zone broadening results from an efficient loss of heat (Joule heat) through the capillary walls. Joule heat is generated by the movement and collisions of ions within the strong electric field gradient. Thus the absence of temperature gradients eliminates convectional broadening. Absence of mass-transfer effects between a stationary phase and a mobile phase eliminates eddy-type broadening. The only significant broadening mechanism is molecular broadening (diffusion). However, high separation speeds on the order of minutes make this broadening negligible.

CE is a very flexible method of analysis. Selectivity in separation can be achieved by changing the buffer composition or by changing the properties of the column that lead to differential interaction of analytes with the column. The differential interactions may be based upon the molecular properties such as size, charge, chirality (nonsuperimposable mirror image), or hydrophobicity. Experimental parameters may also be manipulated to optimize separations. These include varying the applied voltage, electrolytic composition, pH, ionic strength, use of additives, and wall coatings.

CIA is very useful for the separation of inorganic ions and organic acids. Prior to CE, these species were often analyzed using IC. Since these species lack a chromophoric center, they must be detected indirectly using a UV absorbing species which is part of the buffer system. Chromate or imidazole are commonly used for this purpose. Detection occurs when the analyte zone displaces the absorbing species and causes a decrease in ambient background absorbance. This method of detection has relative standard deviations of 1%-2% and is applicable to a variety of species (Table 14). The primary disadvantage to CIA is the ability to measure only the positive or the negative ions. Individual ions have a high degree of mobility, and the electroosmotic flow is not sufficient to counteract the flow of ions to their respective electrodes. Thus only one type of charged species can be determined per analysis.

![Figure 13. Flat flow depiction (left) and laminar flow (right) profile.](image-url)
TABLE 14

Limits of Detection for CIA$^{38}$

<table>
<thead>
<tr>
<th>Anion</th>
<th>Detection limit, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromide</td>
<td>0.38</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.14</td>
</tr>
<tr>
<td>Sulfate</td>
<td>0.17</td>
</tr>
<tr>
<td>Nitrite</td>
<td>0.33</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.34</td>
</tr>
<tr>
<td>Fluoride</td>
<td>0.10</td>
</tr>
<tr>
<td>Phosphate</td>
<td>0.38</td>
</tr>
<tr>
<td>Carbonate</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Other anions analyzed by capillary ion electrophoresis include thiosulfate, molybdate, tungstate, citrate, formate, phosphite, chlorite, perchlorate, carbonate, ethanesulfonate, and acetate.

**Methods of Injections.** Hydrodynamic and electrokinetic injections are the two most common means for quantitative sample injections in capillary electrophoresis. Neither of these methods will be fully discussed, owing to their detail and complex relationship to CE experiments in general. Briefly, both techniques involve the injection of an unknown quantity of analyte, although the concentration can be calculated. The variables of importance include pressure/time (hydrodynamic) and voltage/time (electrokinetic) for each of the injection techniques. Hydrodynamic injection is based on applying a pressure to the sample volume while simultaneously applying a vacuum to the CE drain reservoir. The differential pressure, combined with the lowering of the drain reservoir, results in siphoning of the analyte plug into the capillary.

The electrokinetic method involves the application of a voltage to the injection reservoir with a simultaneous opposite voltage applied to the drain reservoir. The voltage difference across the capillary is generally 3-5 times lower than is used for separation. The analytes enter the capillary through migration and the electroosmotic flow. The main advantage to electrokinetic injection is that high mobility ions are preferentially injected into the capillary.

**Methods of Detection.** Although there are detection challenges imposed by CE, they can be surmounted by modification of the techniques. The most widely used method is UV-visible absorption spectroscopy. On-capillary detection combined with UV-visible absorption spectroscopy allows for high sensitivity and universal detection of many analytes. The elimination of zone broadening, dead-volume, and component mixing, along with direct measurement within the capillary confines, are in large measure responsible for the high separatory resolution afforded by CE.

The optimization of the detection system for CE relies in large measure upon the short optical path defined by the capillary internal diameter. Proper focusing of the optical beam into the capillary cell must allow for optimal light throughput with minimal background light impinging upon the detector element. Optimization for slit width, length, and distance from the capillary are crucial variables which affect the signal-to-noise, linear dynamic range, and the resolution of the
chromatographic data. Table 15 lists several detection methods for CE, along with a description of their sensitivity, strengths, and weaknesses.

As shown in Table 15, there are higher restrictions to linear detection range for these methods than the corresponding HPLC techniques (the linear detection range for CE is generally 0.4 to 0.7 absorption units, while the corresponding range for HPLC is 1.2 to 1.5 absorption units. This is because of the small capillary path length through which the light must be directed.

### TABLE 15

Detection Methods for Capillary Electrophoresis and Detection Limits

<table>
<thead>
<tr>
<th>Method</th>
<th>Mass Detection Limits, moles</th>
<th>Concentration Detection Limit, molar*</th>
<th>Advantages / Disadvantages</th>
</tr>
</thead>
</table>
| UV-Vis Absorption         | $10^{-13} - 10^{-16}$        | $10^{-5} - 10^{-8}$                  | • Universal  
• Diode array offers spectral information                      |
| Fluorescence              | $10^{-15} - 10^{-17}$        | $10^{-7} - 10^{-9}$                  | • Sensitive  
• Usually requires sample derivatization                           |
| Laser-Induced Fluorescence| $10^{-18} - 10^{-20}$        | $10^{-14} - 10^{-16}$                | • Extremely sensitive  
• Usually requires sample derivatization  
• Expensive                                                          |
| Amperometry               | $10^{-18} - 10^{-19}$        | $10^{-10} - 10^{-11}$                | • Sensitive  
• Selective but useful only for electroactive analytes  
• Requires special electronics and capillary modification            |
| Conductivity              | $10^{-15} - 10^{-16}$        | $10^{-7} - 10^{-8}$                  | • Universal  
• Requires special electronics and capillary modification            |
| Mass Spectrometry         | $10^{-16} - 10^{-17}$        | $10^{-8} - 10^{-9}$                  | • Sensitive and offers structural information  
• Interface between CE and MS complicated                            |
| Indirect UV, Fluorescence, Amperometry | 10–100 times less than direct method | — | • Universal  
• Lower sensitivity than direct methods                               |
| Others                    |                              |                                      | Radioactivity, thermal lens, refractive index, circular dichroism, Raman |
* Assumes a 10-nL injection volume.
Although CE has not become a standard technique in the commercial analytical laboratory, there are several experimental variables which make CE adaptable to quantitative analysis of important analytes. Each of these experimental variables adds to the complexity and degree of expertise required. Quantitative analysis peak areas are generally 2% relative standard deviation (RSD) under properly controlled conditions. The factors affecting peak area and peak height include temperature, sample adsorption, injection method, and low sample concentrations. Table 16 lists major factors which must be considered and properly maintained for precise run-to-run results.

### Table 16

<table>
<thead>
<tr>
<th>Factor</th>
<th>Cause/Effect</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature Changes</td>
<td>Changes in viscosity and injection amount</td>
<td>• Thermostat capillary</td>
</tr>
<tr>
<td>Sample Evaporation</td>
<td>Increasing sample concentration</td>
<td>• Cap vials and/or cool autosampler</td>
</tr>
<tr>
<td>Instrumental Limitations</td>
<td>System rise time significant proportion of injection time</td>
<td>• Increase injection time</td>
</tr>
<tr>
<td>Sample Carryover</td>
<td>Extraneous injection</td>
<td>• Use capillary with flat, smooth injection end</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Remove polyimide from end of capillary</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Dip capillary in buffer or water after injection</td>
</tr>
<tr>
<td>Zero-Injection Caused by Simply Dipping the Capillary in the Sample</td>
<td>Extraneous injection</td>
<td>• Cannot be eliminated but can be quantified</td>
</tr>
<tr>
<td>Sample Adsorption to Capillary Walls</td>
<td>Distorted peak shape Noneluting sample</td>
<td>• Change buffer pH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Increase buffer concentration</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Use additives</td>
</tr>
<tr>
<td>Low Signal-to-Noise Ratio</td>
<td>Integration errors</td>
<td>• Optimize integration parameters</td>
</tr>
<tr>
<td>Sudden Application of High Voltage</td>
<td>Heating, thermal expansion of buffer, and expulsion of sample</td>
<td>• Increase sample concentration</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Use peak height</td>
</tr>
<tr>
<td>Electrokinetic Injection</td>
<td>Variations in sample matrix</td>
<td>• Use hydrodynamic injection</td>
</tr>
</tbody>
</table>
As previously described, CE has not received widespread attention in regard to environmental applications. There is an expected increase in method development for CE and related techniques.

**Thin-Layer Chromatography (planar chromatography)**

Thin-layer chromatography (TLC) is a separation technique primarily used for organic compounds, especially polar, thermally unstable, or high boiling compounds. It may be used for sample cleanup prior to GC, LC, or other analytical methods. Alternatively, it may be used by itself as a regular analytical procedure.

As in other chromatographic techniques, TLC yields separation via a continuous series of adsorption partitionings of the analyte between a stationary solid phase and a mobile liquid phase. The solid phase, very often alumina or silica gel, is generally a sorbent material coated as a layer on a hard backing plate of aluminum, plastic, or glass. The dimension of a TLC plate is typically a few centimeters on a side. The mobile phase (eluent) moves through the porous stationary phase by way of capillary action. The migration order of the analytes is inversely proportional to how strongly they adsorb/partition on the stationary surface.

The setup consists of a closed chamber with a thin pool, about 6 mm deep, of the eluting solvent. The bottom edge of the TLC plate dips into the liquid. The chamber atmosphere is saturated with the vapors of the mobile phase. The analytes are first dissolved in a solvent and then applied in very small volumes (10 – 40 nL) to the plate near its lower end. The concentration of the analyte solution ranges from as low as 0.2 mg/L to as high as 10%. Spot sizes less than 1 mm are formed. Smaller spot sizes provide better resolution. The dried plate is placed in the chamber, so that the end closer to the analyte position is dipped in the eluting solution. The eluting solution must wet the stationary phase. Precautions must be taken not to dip the analyte region directly in the mobile phase. The solution moves through the capillary pores of the stationary phase and separates the analytes according to their sorption strengths. When the solvent front reaches to within a few millimeters of the top edge of the plate, it is removed from the chamber. The solvent front edge is marked immediately, and the plate is allowed to dry.

The selectivity of the separation can be extended by developing the plate in two dimensions at right angles to each other, using two different solvents for the two runs. This is referred to as two-dimensional TLC. Thin layer (analogous) chromatography can also be practiced on paper (paper chromatography). Using a special paper developed for chromatography purposes, the solvent runs in a prescribed direction to obtain the most efficient separation.

A recent advancement is high-performance TLC (HPTLC) which improves on classical TLC in three major ways: the quality of the stationary phase, the mode of sample application, and the incorporation of instrumental techniques for detection. The gel particles of the stationary phase are small and are of very uniform packing size so that they form a homogeneous smooth surface. The migration distances are small, and the development times are short. HPTLC produces high resolution chromatograms; sample sizes in the nanogram–picogram range have been analyzed. The use of plates having “concentration zones” leads to better sample alignment, smaller spots, and better resolutions (no streaks). Concentration zones refer to the technique of concentrating the sample mixture before development.
In its classic version, TLC plates are developed by allowing the solvent front to move linearly and vertically up the plate. Recent advances allow horizontal, circular, and anticircular development. The horizontal mode gives better control of the development, improving the overall analytical outcome. Circular development begins with the sample "spotted" at the center of the plate. The developing solvent is made to run in a radial direction on the plate, outward from the spot, resulting in better resolution. In the anticircular mode, the analytes are applied on a larger circle, and the solvent moves toward the center of the circular plate.

The separated zones are identified visually for qualitative analysis or by a scanning densitometer for quantitative purposes. Use of UV/visible light to locate the analyte zones (via fluorescence/absorption) is common practice. The zones may also be scraped and analyzed with any other available technique. A very important identifying marker for planar chromatography is the Rf value, which represents the ratio of the analyte migration distance to the distance which the solvent front has traveled. Comparison of the Rf value with those from standards may be used to identify the analyte components. Molecules may also be derivatized to make them amenable to detection. TLC/HPTLC has been applied in analytical work for PAHs, phenols, surfactants, amines, amino acids, hydrocarbons, herbicides, pesticides, inorganic ions, etc. Detection limits of 0.1–100 ng/spot (UV/Vis absorption) and 0.01–10 ng (fluorescence) have been reported. Relative standard error is 1%–3% with instrumental detection.
APPENDIX C

UV/VIS SPECTROSCOPY PRINCIPLES
UV/VIS SPECTROSCOPY PRINCIPLES

INTRODUCTION

Spectroscopy is the quantitative study and characterization of interactions between light and matter. All spectroscopic techniques involve 1) a source of electromagnetic radiation (light); 2) coupling of the light with the sample via absorbance, scattering, or emission; and 3) quantitative analysis of the intensity and wavelength resulting from that coupling. Spectroscopic measurements can be made quickly and repeatedly since the phenomenon occurs literally at the speed of light. When fast acquisition time is not required, signal averaging can be used to improve the signal-to-noise ratio. In the ultraviolet (10–380 nm) through near-infrared (800 nm) spectral regions, spectroscopy is compatible with light delivery and collection over fiber-optics so measurements can be made with a considerable distance between the sample and the instrument itself.

Spectroscopy can be performed directly on the sample after manipulation of the sample (e.g., by extraction or chemical reaction) or in combination with chromatographic separation techniques. Spectrophotometry refers to a branch of spectroscopy in which chemical manipulations are used to achieve products with the desired spectroscopic properties. Direct measurements are advantageous if the sensitivity and/or selectivity are sufficient. The sensitivity and specificity can be strongly affected by instrumental configuration. Greater sensitivity and specificity often means higher costs for technologically advanced equipment.

An example of the use of spectroscopy is an application that requires a continuous measurement of the concentration of benzene in a gas stream moving through a pipeline. For continuous monitoring, a light source shines at right angles to the flow. A detector is placed at the opposite side of the pipe. The light signal passing through the pipe is modified (attenuated) by the presence of benzene in the stream, and the degree of modification can be related to the benzene concentration. Required detection limits, the expected product of analyte concentration and sample path length, and whether there are interfering species present are all relevant to sample measurement in this example. It might be feasible to detect benzene at a vapor concentration of 1 ppm (v/v) over a path length of 1 m. However, a concentration 10 times lower (for the same pathlength) would probably fall below the limit of detection. The presence of analytes with similar spectral features, e.g., toluene or xylene, is likely to degrade the detection limits and precision of the measurement.

Absorption, emission (including fluorescence), and Raman scattering are the three main subdivisions of spectroscopy. Absorption is an attenuation process. As the light passes through a sample, its intensity is diminished at certain wavelengths. Emission refers to light given off from a sample as molecular or atomic species pass from a higher- to a lower-energy state. The higher energy states may be produced by a light absorption process, although there are other excitation mechanisms such as chemical reaction and thermal excitation. Raman scattering is similar to emission in that the initial excitation is photon absorption.
The three main processes can be schematically illustrated in equation form:

Absorbance  light + ground state → excited state
Emission  excited state molecule → ground state molecule + light
Raman  input light + molecule + ground state → scattered light + molecule in new energy state

Spectroscopy can be applied to both qualitative analysis (answering the question of what species are in the sample) and quantitative analysis (what are their concentrations). The qualitative analysis component is based on the fact that each molecule has its own characteristic spectrum. Analytical spectroscopy aims to identify the presence of specific chemical species and to determine their concentrations. Speciation, selectivity, freedom from interferences, sensitivity, and detection limits are issues of importance.

The width of spectral features (spectral width) is an important factor determining how specific and/or selective a spectroscopic measurement will be. Because atomic transitions are very sharp, that is, they occur in very narrow wavelength bands, a characteristic pattern indicative of what elements are present is easily obtained. Atomic transitions are sharp because they are of sufficiently high energy to exclude the observation of other spectroscopic transitions and are also well separated from each other. Molecular spectroscopies usually do not offer the high degree of narrow wavelength bands associated with atomic spectroscopies. Molecular spectra measure the vibrational and rotational energy levels of molecules. Molecules generally possess many such levels, and hence the spectra tend to be broad and give rise to overlapping features.

**ABSORBANCE SPECTROSCOPY**

The quantitative basis of spectrophotometry (which is the application of absorbance spectroscopy to determine concentrations), is Beer's Law, which states that absorbance is dependent on concentration. Consider light of a certain wavelength incident on a sample. As the light passes through a distance $b$ in the sample, it may become attenuated (lose intensity). If $I_0$ is defined as the incident light intensity and $I$ is the intensity after passing through the sample, the transmittance $T$ is defined as

$$T = \frac{I}{I_0}$$

The transmittance is a number between 0 and 1. The absorbance is defined as the negative (common) logarithm of the transmittance,

$$A = -\log T$$

According to Beer's Law, the absorbance is related to the concentration of absorbing species $C$ by

$$A = \epsilon b C$$
where $b$ is the path length through the sample and $e$ is a constant characteristic of the absorbing species. The recommended term for $e$ is molar absorptivity although the older term, extinction coefficient, is often used.

In Beer's Law, $b$ and $C$ are wavelength-independent, but $e$ is not. A graph of $e$ versus wavelength is distinct for any given compound and is the most fundamental representation of an absorbance spectrum. Changes in pathlength $b$ or concentration $C$ affect the scaling factor of the spectrum, but the shape is unchanged. One can draw an analogy to chromatography. The molar absorptivity (spectrum) in spectroscopy plays the same role as retention time in chromatography; that is, it provides the specific identification. However, in spectroscopy, the overlap of spectral features from different components is much more common and much more of a problem than in chromatography.

The molar absorptivity can be determined by measuring the absorbance of a standard solution of known concentration and pathlength. With this datum, the concentration of an unknown solution can be determined.

Beer's Law is additive: the total absorbance is the sum of the absorbance of individual components. One can therefore write the total absorbance of a mixture as

$$A_{\text{total}} = \sum \varepsilon_i b C_i$$

where $\varepsilon_i$ and $C_i$ are the molar absorptivity and concentration, respectively, of the $i^{th}$ species. The absorbance at a single wavelength is not enough to determine concentrations, but by using absorbance at as many wavelengths as there are chemical components (or preferably at as many wavelengths as possible), the above equation can be inverted to find the $C_i$. Note, however, that the $\varepsilon_i$ must be known as well. Therefore, it is necessary to know which components are present. If there is an additional absorbing species not contained in the database, then the results are adversely affected.

Ultraviolet/visible (UV/VIS), near-IR, Raman, and mid-IR absorptions probe different types of molecular energy levels. UV/VIS absorption monitors electronic transitions, which are usually poorly structured under room temperature solution conditions. In contrast, individual Raman and mid-IR bands, which carry molecular vibration information, may span as little as 0.1% of the whole spectrum. Near-IR spectroscopy monitors overtone and combination vibrations, which have widths intermediate between those in the mid-IR and UV-VIS regions. Fluorescence is an electronic spectroscopy like UV/VIS absorbance and has comparable bandwidths. Atomic emission and atomic fluorescence spectral line widths are “linelike,” similar to atomic absorption linewidths.

The greater the spectral dimension, the more specific an analysis is expected to be. Absorption measurements are one-dimensional. They measure the attenuation of incident light passing through a sample as a function of wavelength. Fluorescence is two-dimensional, since the intensity of the emitted radiation depends both on the incident (exciting) wavelength and the detection (emission) wavelength. Pulsed excitation adds a third dimension, the timescale over
which the fluorescence is emitted. Nonresonance Raman scattering is one-dimensional. However, the intensity of the scattered radiation increases dramatically for certain vibrations as the excitation light approaches an absorbance band; this form is known as resonance Raman scattering, which yields two-dimensional data similar to an excitation emission spectrum.

Absorbance is ideally independent of light source intensity since it is shown by Beer's Law to be expressed as a ratio of incident to transmitted light. Thus, the detection limits for a measurement generally cannot be improved by going to a more intense light source. The amplitude stability of the light source and noise characteristics of the detection electronics are each more significant than the absolute source intensity for absorbance measurements. To achieve low detection limits requires the ability to measure a small change in a relatively large signal. Detectors for the UV/VIS region have very low noise. Source intensity fluctuations can be eliminated with a double-beam configuration, so generally high signal-to-noise ratios result. Near-IR detectors are not appreciably inferior to UV/VIS detectors and the signal-to-noise ratio is very similar. Mid-IR detectors are not as quiet as near IR detectors and issues concerning how much light is delivered to the sample and how well the transmitted light is collected (i.e., light throughput) are important. Atomic absorption sources are hollow cathode lamps or electrodeless discharge lamps constructed from the element of interest. Low-intensity hollow cathode lamps may lead to inferior detection limits for certain elements.

EMISSION SPECTROSCOPY

Emission spectroscopy examines the light that is given off by a sample as excited atoms or molecules drop from a higher- to a lower-energy state. The excited atoms or molecules can be created in many different ways: via photoexcitation, chemical reaction, or in a flame. The emission processes are named according to how the excited species are generated and the nature of the photon emission process, such as chemiluminescence, fluorescence, and phosphorescence. The emission spectrum has a characteristic spectral shape, (distribution of intensity versus wavelength) which can be used for compound identification. However, there is no equation analogous to Beer's Law, and concentrations can only be established by standards.

Fluorescence and Raman spectroscopies are powerful processes whose signal strengths are directly proportional to the excitation flux. If greater signal is required, it can be achieved with greater excitation intensity. Fluorescence and Raman spectroscopies, are ideally zero-background, although some background signal arises from physical scattering off the sample container, from particular matter in the sample, or Raman scattering from the solvent. Nevertheless, it is accurate to say that in fluorescence and Raman spectroscopies, one measures a relatively small signal against an even smaller background. Because the detected signal amplitude is relatively small in fluorescence compared to absorption (and much lower in Raman), signal-to-noise ratio and precision tend to suffer. In general, the experimental configurations and instrumentation for fluorescence and Raman are very similar. Figure 1 illustrates a typical layout for a fluorescence/Raman spectrometer in which a sample is irradiated with a certain wavelength and subsequently monitored for emission.
The vibrational spectroscopies (mid-IR, near-IR, and Raman) are completely general. Every organic molecule, e.g., a chlorinated solvent, explosive, PCB, polycyclic aromatic hydrocarbon, alkane, possesses vibrational spectra. It is also true that every molecule will exhibit electronic transitions at sufficiently short wavelengths. The restriction to wavelengths compatible with fiber transmission properties and light source availability (e.g., longer than 240 nm) for fiber-optic transmission eliminates nonaromatic hydrocarbons and chlorinated solvents as candidates for direct electronic absorbance measurements. The classes of molecules that exhibit fluorescence (which requires an initial photon absorption) is even smaller. However, it does include the polycyclic aromatic hydrocarbons.

**RAMAN SPECTROSCOPY**

Raman spectroscopy probes the vibrational levels associated with the ground electronic state. These ground vibrational levels dictate or identify the molecule. Energy is either lost or gained by molecules during the process, and results in the scattering of light, which is either higher in frequency (anti-Stokes scattering) or lower in frequency (Stokes scattering). Raman scattering is a concerted process in which no measurable time delay exists between the absorption and the emission of light. For this reason, it should not be considered a form of fluorescence, which involves a given excited molecular state of the analytes and is a time-dependent process. Raman scattering does not directly involve higher-energy molecular states in the scattering process. Thus the ground or lower-lying states are the relevant energy states that dictate the frequency of scattered light.
Scatter of incident radiation that is not converted to a different frequency is known as Rayleigh scattering. Figure 2 demonstrates relative Raman scattering intensities of the Stokes, anti-Stokes, and Rayleigh components.

Raman spectroscopy has traditionally been reserved for species that do not fluoresce or that show appreciable absorption. Raman techniques are generally easy to implement and with the ever increasing advances in light sources and detectors, are providing greater flexibility and hence greater use in diverse applications. The primary disadvantage to Raman scattering is the low sensitivity of the technique due in part to background fluorescence and low scattering efficiency. As a result, there has been limited use of Raman spectroscopy in environmental applications. Raman spectroscopy will likely receive greater attention in regard to environmental applications with the advent of tunable near-UV light sources such as lasers and optical parametric oscillators (OPOs), more sensitive and versatile detectors, the applications of fiber optics for light transmission/collection, and chemometric techniques for data analysis. Likely applications will include in situ detection of nonaromatic chlorinated solvents and other species not readily measured with traditional in situ techniques.

SPECTROPHOTOMETRY

Spectrophotometry is a spectroscopic technique used in the analysis of light absorbing compounds. Colored compounds absorb light from the UV/VIS or IR region of the spectrum. The degree of absorption of light is proportional to the concentration of the colored species through Beer's Law (Appendix C). Concentration is measured by measuring absorbance, and determinations are made through indirect methods. All spectrophotometric methods require calibration curves with standards.

Figure 2. Depiction of the various Stokes, anti-Stokes emissions. Rayleigh scattering accounts for the large emission at the fundamental wavelength.
Several types of spectrophotometric detectors are available. Fixed wavelength detectors irradiate the eluent with radiation of a single color, for example, a mercury lamp irradiating at 254 nm. Several fixed wavelengths may be employed in which each wavelength is used separately. Choosing different wavelengths increases sensitivity and selectivity. A monochromator is used with a sample that produces light spanning a large spectral range (continuum source) when variable wavelents are being employed. Diode arrays, charge-coupled devices, and vidicon tubes are used with continuum sources to collect the absorption spectrum of the eluting analytes. In such cases, the acquisition of the spectrum allows for quantitative and qualitative analysis.

Fluorimetric detectors are used to detect analytes capable of exhibiting luminescence upon irradiation, an extremely sensitive technique. Filters obtain monochromatic light for irradiation of the eluent. Lasers, in conjunction with optical fibers to collect and irradiate light, are also used for fluorescence detection.

ATOMIC ABSORPTION

The principal analytical techniques for the detection and quantitation of metals in environmental samples are atomic spectroscopy (absorption and emission), chromatography, colorimetry, and electrochemistry. Atomic spectroscopy methods are the most often applied and are emphasized in this section.

Metallic elements in ore deposits, sediments, and soils generally exist as cations (positively charged species) combined with anionic (negatively charged) partners such as oxide, sulfate, sulfide, carbonate, or chloride. Gold, silver, copper, and platinum, which can be found as free metal deposits, are the exceptions. Mercury can be found in a variety of states, a common form being covalent bonding of mercury to an alkyl moiety (e.g., sulfide). Many metals exhibit more than one charge state, which is also referred to as an oxidation state. For example, iron is commonly found in either the ferrous (+2) or the ferric (+3) charge states. In many cases, the analytical methods reveal only the total metal content, irrespective of oxidation state. However, if the toxicity/hazard is highly dependent on oxidation state, oxidation-specific methods may be required. For example, hexavalent chromium (+6 charge state) is much more toxic than the other chromium charge states. Accordingly, specific regulatory limits may be applied.

The metallic elements can be found in the environment in solid forms, dissolved in solution, or both. Mercury can exist as a neutral atomic species or as a covalently bonded species. Moreover, both the free metal and bound forms, including some which are ionic, exhibit significant volatility.

If the oxidation state information is not required, the sample is usually subjected to chemically harsh conditions by using an organic compound and the carbon–hydrogen–nitrogen (CHN) analysis technique. The CHN technique involves combustion of a known mass of organic sample under conditions such that all carbon, regardless of how the atoms are bonded, is converted to carbon dioxide, all hydrogen to water vapor, and all nitrogen to elemental nitrogen.
gas. The gaseous products are collected and quantitated. The quantification method is usually a simple process of weighing the samples. Simple calculation allows the conversion of grams of carbon dioxide product into moles of carbon dioxide, which equals the moles of carbon in the original sample. Another mole conversion turns this datum into the grams of carbon in the original sample and therefore into the weight percent of carbon in the sample.

The CHN technique is applied to newly synthesized compounds to verify that the desired product has been obtained. Of course, this approach is not of interest for environmental analysis. It makes a big difference whether the 1 mg/L of carbon in a groundwater sample arises from benzene or from humic acid. Speciation to at least some degree is almost always necessary. That similar considerations generally do not apply to metal analysis make the technique more suitable for environmental applications in this case.

The most widely used, precise, accurate, and sensitive methods for metal analysis are those in which the samples are first atomized and then detected by spectroscope. In the atomization process, the sample is subjected to sufficiently energetic conditions to break any chemical bonds to the metal atoms. Such conditions are almost always sufficiently energetic to simultaneously vaporize the material, with the net result that the analyte is transformed into a "free" gaseous species.

None of the atomic spectroscopic methods yield concentrations directly or in an absolute sense. The concentrations are invariably established via a comparison of the spectroscopic signal for the sample with that of a standard of known concentration. The running of standards yields the proportionality constant between experimental signal (intensity) and concentration and establishes detection limits and analytical precision. The amount (total mass or volume) of both the sample and the standard introduced into the instrument must be known precisely. For atomic spectroscopy, the usual procedure for liquid samples is to inject or aspirate a known volume. Solid samples are first converted to the liquid phase before being injected.

It is not necessary that every metal atom of the sample be transferred into the gas phase, nor is it essential that all gas-phase atoms be in the same form. A wide distribution of neutral and various cationic forms may result from the atomization step. It is critical, however, that the distribution be highly reproducible, since the concentrations must be related to the signals of standards of known concentration. Any variations in atomization efficiency between the sample and standard are categorized as matrix effects, which are discussed below.

Until a few years ago, the atomization step was always followed by spectroscopic detection. The spectroscopic transitions of metal atoms and ions in the gas phase are extremely sharp (that is, the wavelength spread of an individual transition is very narrow), and the transition wavelengths are known to have a high accuracy. These factors lead to high selectivity and sensitivity of atomic spectroscopic analysis. In the past few years, an alternative detection technique, mass spectrometry, has been teamed with inductively coupled plasma as the atomization source. Inductively coupled plasma–mass spectroscopy (ICP–MS) is included as a form of atomic spectroscopy (Appendix C).
The four generic atomic methods are atomic absorption, atomic emission, atomic fluorescence, and ICP-MS. More practically, categories are listed as flame atomic absorption spectroscopy (flame AAS), graphite furnace atomic absorption spectroscopy (GFAAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS). Other atomic methods exist but occupy niche areas. Figure 3 is a simplified flow chart for flame AA and ICP. The instrumentation for flame AA and graphite furnace AA is virtually identical except for the atomization procedure. Emission or mass spectrometry detection can be employed with inductively coupled plasma.

**Flame and Graphite Furnace**

Like all other light absorption techniques, atomic absorption analysis is based on Beer's law (Appendix C). The intensity of light transmitted through the sample vapor is measured in the absence ($I_0$) and in the presence ($I$) of analyte. The ratio $I/I_0$ decreases relevant to the increase in the number of absorbing species in the pathlength of the light. In principle, one can obtain the concentration of an analyte directly from the absorbance measurement if the pathlength and molar absorptivity are known. Several practical problems can negate this ideal situation, some of which are listed below:

- The concentration of a metal in a solid (soil) or liquid (water) sample is desired, even though the actual absorbance measurement is made on a gaseous phase. Thus, the efficiency of the atomization process must be questioned. Note that during the atomization process, the metal may enter into any one of a large number of neutral and ionic states.

![Diagram of atomization process](image_url)

**Figure 3.** Shown above are the steps involved in the atomization procedure for performing molecular or atomic spectroscopy on analyte samples.
• Beer’s Law assumes a homogeneous distribution of analyte throughout a sample of well-defined pathlength. The homogeneous distribution condition is virtually impossible to obtain in atomic absorbance.

• The molar absorptivities are a function of temperature, which reaches extreme conditions in the AA environment. Nonetheless, Beer’s Law can still be applied in a modified form,

\[ \log \left( \frac{I_0}{I} \right) = k \text{ [conc.]} \]

where the proportionality constant \( k \) must be determined by experiment under the same conditions as those for which the unknowns are measured. A calibration curve is measured for different concentrations.

Figure 4 illustrates a schematic flame atomic absorption apparatus. The main system components are the light source, the "sample cell" in which the atomization occurs, and the light detection system. The usual light sources for atomic spectroscopy are hollow cathode discharge lamps (HCLs) or electrodeless discharge lamps (EDLs). Both yield discrete frequencies of light (line spectra) characteristic of the element under investigation. An HCL consists of a hollow cylindrical cathode containing the element of interest in a low-pressure buffer gas (1–10 Torr) of neon or argon. The lamps are excited by a low-voltage source, operated either AC or DC, at a few hundred volts and a few milliamps current. Atoms become ejected (sputtered) from the surface of the hollow cathode and are excited by collisions with the buffer gas in the resulting glow discharge. The light emitted as these atoms relax to their ground states is at wavelengths that closely match the absorbance wavelengths of elements in the atomization plume.

If the light from the hollow cathode discharge is at the wavelength of the desired spectroscopic transition, the light transmitted through the plume with a photomultiplier tube or similar photodetector can be directly measured. However, a monochromator is generally required for resolution sharpening since the light output from an HCL is distributed over several wavelengths. In addition, there are lines generated from the fill gas and possibly others from impurities in lower-quality lamps. The wavelength(s) that offer the best sensitivity and freedom from interferences for a given element are well known. These are not necessarily the most intense lines since detector noise usually does not serve as the limiting factor for low analyte detection. (There are a few elements for which low lamp intensity adversely affects detection limits.) Selection of the optimum hollow cathode line depends on other elements that may be present in the sample, especially if the other element shows absorption near the chosen wavelength. If so, an adjustment should be made to the monochromator slit width or a different wavelength should be chosen.

A specific HCL for the element to be analyzed must be used. Owing to this element specificity, simultaneous multielement analysis on a single sample is difficult, and sample throughput is lower than in competing techniques that use emission or mass spectrometry detection. For multielement atomic absorption analysis on a given sample, three operations per element are required: selection and optical alignment of the appropriate HCL, setting the...
monochromator to the appropriate wavelength, and resolution sharpening. Some commercial
units have incorporated turrets or carousels of HCLs that automatically interchange lamps in
order to shorten analysis time. Even greater efficiency is obtained with a novel instrument in
which up to five lamps can be mounted simultaneously, each with separate detectors.

**Atomization Procedure**

The process by which chemical bonds are broken and the analyte is transferred to the gas
phase is key to atomic spectroscopy. Since the concentrations of the unknown are related to those
of the standards, the highest possible precision in delivering a reproducible amount of sample to
the instrument is required. This is a common theme which applies, for example, to gas
chromatography and high-performance liquid chromatography (HPLC). Invariably, the sample
must first be converted to the liquid state before aspiration (nebulization) of a known volume into
the instrument.

The analytes in flame atomic absorption spectroscopy are aspirated into the flame of an
air–acetylene or nitrous oxide-acetylene mixture. The flame burner head is slot-shaped and
aligned so that the light beam from the hollow cathode lamp passes along the long axis of the
flame. As the aerosol sample contacts the flame, the high temperature breaks the chemical bonds
of the analyte; note that the flame is effectively the "cell" holding the analyte.

Flame atomic absorption is a respected technique with many advantages. Ease of use,
relatively low system cost, high precision, and usefulness at high concentrations makes it the
method of choice for determination of major constituents when one or very few elements are of

![Diagram of flame atomic absorption apparatus](image)

**Figure 4.** Flame atomic absorption apparatus. Radiation is separated using a monochromator and
detected with a photomultiplier tube.
interest. The sensitivity and analytical range of the technique are limited, however, because the burner-nebulizer system of a flame AA unit is not very efficient. Most of the sample does not reach the flame.

Graphite furnace atomic absorption spectroscopy differs from flame AA in the manner in which sample is introduced and vaporized. In GFAAS, also referred to as electrothermal atomization, a small sample volume (about 20 μL) is directly introduced into a graphite tube. A preprogrammed set of heating steps serve to remove solvent and organic "ash" material, and vaporize matrix components, and finally atomize the remaining sample. Accordingly, interferences from the matrix and the solvent are minimized. Because the atoms of analyte remain in the graphite tube, efficiency is greatly enhanced over flame AA, where little of the sample reaches the flame. The total absorption signal from its appearance to its disappearance is measured instead of the peak height as in other techniques.

The nonreactive atmosphere (argon/nitrogen) and the strongly reducing character of the graphite allow for greater concentration of atoms in the atom plume. Also, these atoms are confined to a small volume for a long time. These factors increase the signal-to-noise ratio and thereby increase the sensitivity and lower the detection limit by a factor of roughly 100 when compared to flame AA.

A few elements, referred to as refractory elements (e.g., Ba, Y, Mo), are not compatible with analysis by flame AA and GFAAS because they form oxides with such high melting points that very few free atoms are generated in the plume. Nitrous oxide-acetylene flames yield better results for these elements than do air-acetylene flames, owing to the higher temperatures achieved in the former. A common practice to overcome this limitation is to generate volatile hydrides of the refractory elements, which can be introduced as a gas into the flame via a stream of inert gas. In particular, arsenic, selenium, antimony, bismuth, germanium, tellurium, tin, and lead show improved detection limits by the hydride method in comparison to direct flame AA. Detection limits are even better for these elements with the hydride technique than by GFAAS. On the other hand, a larger volume of sample is required for the hydride method.

For discussion on mercury analytical techniques, handling problems, etc., see N.S. Bloom's Gas Research Institute topical report, "Sampling and Analysis for Mercury in Environmental Media of Importance to the Natural Gas Industry," Dec. 94.

Atomic Emission/Fluorescence Spectroscopy

Light emission is a complementary process to light absorption. Light absorption results in the disappearance of a photon and the corresponding elevation of an atomic or molecular species to a higher energy state. In light emission, the atomic or molecular species spontaneously passes from a higher energy state to a lower energy state with the liberation of a photon. The energy of the absorbed/emitted photon matches the energy difference between the two molecular/atomic energy states.
Light emission analyses are conventionally subdivided into atomic emission and atomic fluorescence categories, although this subdivision is imprecise. The practical distinction is whether an external light source is used to create the excited atomic states from which emission occurs. If so, the term atomic fluorescence is applied. If no external light source is used, the term atomic emission is applied. Most atomic emission is fluorescent by nature.

Atomic fluorescence occurs when analytes are excited with a monochromatic external light source which introduces the same specificity as seen for the absorption methods. The wavelength-specific emission (fluorescence) introduces additional selectivity. Ideally, the only emission signal in atomic fluorescence occurs for those species that have first absorbed a photon. The emission spectrum that results is ideally simple and uncluttered. In reality, the background emission from those species that have not been photoexcited, however small, is not inconsequential.

The standard optical arrangement in atomic fluorescence employs detection of the light emission at right angles to the direction of irradiation from the source (Figure 1). This arrangement minimizes the collection of scattered exciting light by the detector. The ideal excitation source is one that excites only the analyte of interest. Thus HCLs, ELDs, and metal vapor lamps have all been employed. However, all of these also suffer from low intensity. Today, the availability of tunable lasers has extended atomic fluorescence analysis to a very sensitive technique, laser-excited atomic fluorescence. Along with high sensitivity, however, comes the need for highly trained operators and specialized instrumentation.

In contrast, the instrumentation for conventional atomic emission is much like that of atomic absorption, but the primary light source, that is, the HCL, is eliminated. The atomization step must also supply the additional energy necessary to create excited atomic states. The earlier excitation sources were simple flames, which generally lacked the energy needed to create sufficiently high populations of excited states. Other types of arc/spark excitation have been introduced, but have faded from prominence with the development of inductively coupled plasmas.

**Inductively Coupled Plasma (ICP)**

With the introduction of ICPs, atomic emission became a widely used analytical technique. ICP-AES is comparable in sensitivity to flame AA, but is easily adapted to multielement determinations. As many as 40 elements per minute can be determined in an individual sample.

The ICP is usually an argon plasma (ICAP) created by the coupling of a radio-frequency (rf) field tangent to a flowing stream of argon gas in the annulus between two quartz tubes. The emerging plasma from the ICP "torch" (Figure 5) has a toroidal (doughnut) shape, and the sample is introduced axially in the center of the toroid. An electrical discharge creates electrons and ions, which collide with neutral atoms as they follow their path through the rf field. The collisions raise the temperature of the plasma to approximately 8000°C, about 3 times the temperature in a flame with conventional flame AA. The elements of the sample, introduced into the plasma, are completely atomized and brought to various states of ionization. Consistent sample introduction
Radio-frequency coils induce a discharge within the confines of the vapor discharge. This is crucial to the accuracy and precision of results. Common methods are pneumatic and ultrasonic nebulation.

With ICP-AES, the intensity of light emitted at each frequency is proportional to the concentration of the analyte. The spectra produced from ICPs are very rich in spectral lines. This necessitates the use of narrow slits on the emission monochromator in order to discriminate the narrow and close-lying emission lines. The argon carrier gas generates a high level of emission background. Compared to atomic absorption, performance demands on the emission monochromator are much higher. A higher level of operator skill is required to discriminate between the "analytical lines" and the unwanted emissions. Instrument and operator costs increase.

Method development for real samples is difficult because of the high density of spectral lines in plasma emissions (including DC and microwave) and the complex background emission from the argon carrier gas. Rare earths and elements such as nickel, uranium, and iron generate highly complex spectra. Organic, corrosive, or concentrated samples eventually damage the plasma torch, which must be replaced regularly.

The high plasma temperature in an ICP efficiently generates singly charged monatomic ions. Since one-unit resolution is satisfactory, the emission monochromator of an ICP-AES unit is replaced by a simple quadrupole mass spectrometer for ICP-MS. In most ways, the ICP-MS and the ICP-AES operate alike.
The sample introduction in ICP–MS and ICP–AES are the same. The ions produced in the ICP are introduced into the MS (quadrupole mass filter) via a plasma–vacuum interface (PVI). A second "skimmer" cone actually samples the ions and directs the ion beam to the detector.

ICP–MS yields sensitivities comparable to or lower than GFAAS and is capable of simultaneous multielement analysis. The ion current/charge produced by the ionized analytes is the monitored signal. The high-energy rf source eliminates the matrix effects and is an efficient ionizing source. One analyte species is capable of generating hundreds of spectral lines in ICP–AES, and a given sample with many analytes will generate many thousands of lines. In comparison, monitoring the mass of the species literally reduces MS spectra to few lines (isotopes and some interelement compounds) per analyte. Overall the number of lines detected is reduced from thousands to a few hundred. The interferents in ICP–MS are few, but not completely absent. Most interferents are ionized compounds formed by the reaction between the analyte and the argon carrier gas.

Atomization Procedures for Atomic Emission/Fluorescence

The analytes in DC arc AA spectroscopy are excited in a DC arc, which is created between two graphite/carbon electrodes. The electrodes operate in either air or other gas mixtures. One of the electrodes contains the analyte. The arc plasma vaporizes and excites the analyte. A relatively small amount of the sample enters the plasma in DC arc jets. The temperatures in DC arc vary from 5000° to a maximum of 6000°C. The background is very intense, degrading the detection limits of the analytes. Detection limits depend directly on sample composition, arc conditions, and the optical system. Simultaneous multielement analysis is possible with this technique.

In AA spectroscopy, an AC spark discharge vaporizes and excites the analyte atoms. Multielement determinations are possible. Detection limits are poor compared to the DC spark method, but the reproducibility of AC sparks is superior. The effective temperature is much higher, and the spectra generated are more complex due in part to the presence of ions.

Rf energy coupled capacitively to an inert gas flowing through a cavity (microwave cavity) generates a plasma referred to as a microwave-induced plasma (MIP). As an excitation source, it is very similar to ICPs. Detection limits of MIPs more closely compare to DC arc plasmas.

Another developing technique is that of the laser microprobe. A sample is vaporized when it is the focus of a laser pulse. The passage of the vapor plume initiates a spark across the gap of two electrodes located above the sample, further exciting the analyte species. The emissions from such a system can be analyzed for multiple elements. The advantage of this technique is its utility with small samples.

SELECTION OF THE PROPER SPECTROSCOPIC TECHNIQUE

The performance characteristics of flame AA, GFAA, ICP–AE, and ICP–MS are complementary. The technique of choice is based on criteria regarding detection limits, analytical
working range, sample throughput cost, interferences, ease of use, and existence of proven methodology. An experienced analytical chemist must be consulted.

**Detection limits**

The detection limit of a given method obviously plays an important role. If the detection limit is above that required by a given problem, then time-consuming and expensive preconcentration steps are required, which can degrade precision. Table 1 is a general overview of the detection limits ranges for ICP–MS, GFAAS, ICP–AES, and flame AA. Usually GFAAS and ICP–MS provide the lowest detection limits. Table 2 compares limits-of-detection values for elements of interest to the gas industry.

**TABLE 1**

<table>
<thead>
<tr>
<th>Atomic Spectroscopy Technique</th>
<th>LDRs, μg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technique</td>
<td>Detection Limit Range, μg/L</td>
</tr>
<tr>
<td>ICP–MS</td>
<td>0.01–1</td>
</tr>
<tr>
<td>GFAAS</td>
<td>0.01–1</td>
</tr>
<tr>
<td>ICP–AES</td>
<td>1–100</td>
</tr>
<tr>
<td>Flame AA</td>
<td>1–1000</td>
</tr>
</tbody>
</table>

**Analytical Working Range**

To measure samples of different concentrations without changing the methodology, a wide analytical working range (AWR) is desirable. Just as preconcentration may be required if the detection limits are not sufficiently low, dilution may be necessary to get concentrations into the analytical range. In this regard, the ICP–AES and ICP–MS methods are distinctly superior to the AA techniques. Table 3 lists AWRs of the most common atomic absorption and emission techniques.

**Sample Throughput (Operating Cost)**

Sample throughput is essentially a cost concern. Operating cost in regard to personnel depends on the chosen analytical technique and instrumentation. Analysis demands must be carefully examined prior to purchase of the instrument. A qualified lab manager will be able to determine which techniques are most suitable to a particular situation and what instrumentation and personnel are needed to accomplish the analysis. For example, flame AA produces very high sample throughput for single element determinations (about 10 seconds per determination), but this advantage is largely lost for multielement analyses. Even when flame AA is used for multielement determinations in automated systems, the standard practice is to analyze all samples.
for a given element, then to adjust for the next element and to again measure all samples. Such a procedure can become very cumbersome in comparison to the inherently multielement capability of AES and ICP–MS methods. Sample throughput in GFAAS is even lower, owing to the time taken up by the thermal programming to remove solvent and matrix components, about 2–3 minutes per determination. However, this time estimate is for the actual experimental measurement, which is only a fraction of the total time. Sample digestion, preconcentration, dilution, and running of standards must also be performed.

### TABLE 2

Detection Limits of AA Techniques

<table>
<thead>
<tr>
<th>Element</th>
<th>Flame AA</th>
<th>Hg/Hydride</th>
<th>GFAA</th>
<th>ICP Emission</th>
<th>ICP–MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>150</td>
<td>0.03</td>
<td>0.5</td>
<td>30</td>
<td>0.006</td>
</tr>
<tr>
<td>Boron</td>
<td>1000</td>
<td>45</td>
<td>3</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>Barium</td>
<td>15</td>
<td>0.9</td>
<td>0.15</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>1.5</td>
<td>0.03</td>
<td>0.15</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.8</td>
<td>0.02</td>
<td>1.5</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td>3</td>
<td>3</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>1.5</td>
<td>0.25</td>
<td>1.5</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>5</td>
<td>0.3</td>
<td>1.5</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Potassium</td>
<td>3</td>
<td>0.02</td>
<td>75</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Lithium</td>
<td>0.8</td>
<td>0.15</td>
<td>1.5</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Magnesium</td>
<td>6</td>
<td>0.8</td>
<td>6</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>Mercury</td>
<td>300</td>
<td>0.009</td>
<td>1.5</td>
<td>30</td>
<td>0.004</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>45</td>
<td>0.2</td>
<td>7.5</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>6</td>
<td>0.8</td>
<td>6</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>15</td>
<td>0.15</td>
<td>30</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>Selenium</td>
<td>100</td>
<td>0.03</td>
<td>0.7</td>
<td>90</td>
<td>0.06</td>
</tr>
<tr>
<td>Strontium</td>
<td>3</td>
<td>0.06</td>
<td>0.075</td>
<td>0.0008</td>
<td></td>
</tr>
<tr>
<td>Vanadium</td>
<td>60</td>
<td>0.3</td>
<td>3</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>1.5</td>
<td>0.3</td>
<td>1.5</td>
<td>0.003</td>
<td></td>
</tr>
</tbody>
</table>

1All detection limits are given in micrograms per liter (ppb) and were determined using elemental standards in dilute aqueous solution. All detection limits are based on a 98% confidence level (three standard deviations).
Analytical cost is reflected in the price of the chosen instrumentation. There is wide variation in instrument cost. A simple flame AA unit can be purchased for as little as $15,000. Accessories for automated analysis (lamp carrousel, for example) can dramatically increase the initial cost. The ICP–MS instruments can run as high as $200,000. To justify such a large expenditure, very high sample throughput requirements are necessary. GFAAS and flame AA are comparable in cost. ICP–AES carries the widest range of acquisition cost – from $30,000 to $150,000.

Required operator skill and experience and the availability of suitable methods for the analytical problems of interest are part of the decisive criteria. The flame AA technique makes the least demand on the operator. Precision is very high and the methodology has reached a very refined stage. On the other hand, ICP–MS is the newest of the atomic techniques and requires a high level of training. GFAAS and ICP–AES fall between the extremes of flame AA and ICP–MS.
APPENDIX D

TOTAL PETROLEUM HYDROCARBON MEASUREMENTS
TOTAL PETROLEUM HYDROCARBON MEASUREMENTS

Action limits and environmental regulations, particularly for fuel-related substances, are often written in terms of total petroleum hydrocarbon (TPH) concentrations. TPH methods acknowledge that compound-specific analysis of bulk products such as gasoline or diesel is impractical, perhaps even impossible. Although common terminology implies that unleaded gasoline, different diesel grades, or jet fuel have specific and known chemical compositions, the reality is that each one contains detectable amounts of several hundred hydrocarbons. The composition is further influenced by refinery conditions, which are adjusted according to the source of crude product being refined, the current economic conditions, time of year, and destination of the product.

Once in the environment, the various chemical compounds will not degrade or change at the same rate. Weathering is the “catch-all” phrase for how the composition is affected, especially in the outside environment. In addition, the environmental or health risks of all the compounds are not the same. All of the risks or dangers of chemical compounds have not yet been established. The risks that have been ascertained vary greatly. The case could be made that no method for petroleum hydrocarbons can truly be compound-specific, owing to the enormous number of distinct chemical species that are encountered.

TPH methods can be class-specific (e.g., for gasoline or diesel) but are never compound-specific like gas chromatography–mass spectrometry (GC–MS). Compound-specific methods, primarily GC–MS (Appendix B), are very expensive and require expert interpretation. The challenges with this type of method are the handling and interpreting of too much information. The TPH methods reduce all information to a single number, a concentration. However, there is the technical disadvantage of losing analyte-specific detail in the analysis.

Among the petroleum hydrocarbons are aliphatic (straight chain and branched alkanes) and aromatic groups (BTEX [benzene, toluene, ethylbenzene, and xylene], alkyl benzenes [C₆–C₉], and PAHs). The name petroleum hydrocarbons is distinctive. Strictly speaking, hydrocarbons are compounds that contain only carbon and hydrogen, but the term is loosely applied to compounds that are predominantly but not exclusively formed of carbon and hydrogen. Thus, plant material (leaves, fats, etc.) containing heteroatoms such as oxygen and nitrogen can be considered hydrocarbons for purposes of TPH analyses.

There are two main categories of TPH methods: infrared measurements (Appendix C) and gas chromatography (Appendix B), each of which offers very different results. TPH methods are predominantly applied to soil samples, although water samples can also be analyzed. The organic compounds must be separated from the soil matrix prior to actual analysis. IR measurements often utilize freon in the extraction, which contains no C–H bonds and can be done with supercritical fluid extraction. Methylene chloride or SFE is generally used in the GC version. TPH analyses are designed to be fast and simple. Thus, there is a strong interest in fast extractions such as ultrasonic agitation. However, the most volatile organic compounds (BTEX) are easily lost during this process.
The IR process relies on the C–H absorbance in the vicinity of 3.3 microns (3000 cm⁻¹). Since absorbance is proportional to concentration, the proportion factor is established by calibration (Section 4.2). The 418.1 TPH method used in the United States measures only one kind of C–H stretching vibration, the –CH₂– group (methylene). Note that straight chain alkanes are particularly rich in methylene groups. However, CH₃ (methyl) groups and -CH= groups can also be present and absorb at different wavelengths. Thus, if the calibration solution is "richer" in –CH₂– groups than the unknown, the measured values will be biased to lower concentrations away from the true value.

The other main limitation of 418.1 is that nonpetroleum hydrocarbons, such as are found in the organic fraction of the soil, also contain C–H groups that contribute to the TPH signal. Some delineation can be made by using silica gel to remove the more polar compounds that contain oxygen or nitrogen groups. Sometimes this method is referred to as TRPH (total recoverable petroleum hydrocarbons), and the method where the silica gel absorption is not used is referred to as total oil and grease. A further disadvantage of the TPH infrared methods is that the measurement simply gives a number, the absorbance or transmittance through the extractant solution. No information is available in regard to what is contributing to the absorbance reading. For example, the absorbance could be appreciable if small particles pass through the extraction and filtering steps and cause light scattering. The scattering of light is discerned by background measurements on known uncontaminated soil or by using an instrument that measures at more than one wavelength. For example, the instrument could be tuned to 4000 cm⁻¹, where absorbance is very low in almost all compounds. The German DIN method (EPA equivalent) uses three wavelengths in the measurement, thereby providing an added degree of security.

The GC methods detect only compounds that are volatile enough to pass through a GC column. They will not work, therefore, for very heavy products such as tar or asphalt. Also, the GC methods give a very complicated chromatogram. There is added information in the distribution of the chromatogram intensity as a function of elution time. Generally, a flame ionization detector (FID) (Appendix B) is used to give a total carbon response. Conventional practice calls for the analyst to report the integrated intensity between two preselected retention times. The retention time is proportional to carbon number, so the retention time window can be selected to reflect an estimate of carbon number or fuel type. Thus, one sees reference to analyses of diesel-range organics or gasoline-range organics, or equivalently, total petroleum hydrocarbon as diesel or as gasoline. Of course, analyses in terms of TPH-gasoline or TPH-diesel presupposes identification of the product. The degree of certainty with which that identification can be made is affected greatly by weathering processes.

The steps of a total petroleum hydrocarbon measurement are as follows:

Calibration → sampling → extraction → measurement

The extraction is generally performed with a solvent that is sonicated with the soil sample. The purpose of the solvent is to dissolve or "pull" the species of interest from the soil sample into the solution phase, from which they can be measured via spectroscopy or chromatography. The calibration step is designed to relate the instrument response to a concentration. The 418.1
reference standard is a mixture of 37.5% hexadecane, 37.5% isoctane, and 25% benzene (Table 1).

<table>
<thead>
<tr>
<th>Component</th>
<th>-CH₃</th>
<th>-CH₂-</th>
<th>-CH-</th>
<th>-CH=</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexadecane</td>
<td>2</td>
<td>14</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Isooctane</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Benzene</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>6</td>
</tr>
</tbody>
</table>

TABLE 1

Each functional group in Table 1 is associated with absorbance in a characteristic wavelength range. Interestingly, the aromatic -CH- stretching region is at higher frequencies than 3000 cm⁻¹. As a result, many instruments typically used for 418.1 TPH measurements are not sensitive to the rings of the molecule. However, the aromatics are often substituted with alkyl groups containing CH₂ and CH₃ groups that do absorb at an average of 2930 cm⁻¹. The methane, methylene, and methyl groups absorb in the 2850–3000 cm⁻¹ range. A narrow wavelength region is monitored in order to maintain selective detection and hence sensitivity.

The infrared spectra of diesel fuel, gasoline, motor oil, jet fuel, and coal tar are shown in Figure 1, which demonstrates that 2930 cm⁻¹ is a good compromise wavelength. Note that the absorbances for the same concentrations can differ appreciably, indicative of a differential response that could lead to an error of as large as 40+%. A comparison of the hexadecane and isoctane spectra is shown in Figure 2.

![Figure 2. Infrared spectra of hexadecane and isoctane solutions. Wavelengths are given in wavenumber values.](image-url)
Because no two batches of the same petroleum product are the same, and since they are further modified when they are released into the environment, it is difficult to design a method that is applicable to all situations that may be encountered. Since the EPA generally excludes petroleum contamination from RCRA actions, TPH analysis has been left to the individual states. Each state has its own 8015 procedure. The Modified Method 8015 is a last-ditch effort to use EPA methods for the analysis of petroleum hydrocarbons. These methods are constantly changing as the regulators in each state become more familiar with the complexities of petroleum hydrocarbons and the limitations of the methods they have promulgated.

The Modified 8015 methods generally use a gas chromatograph with FID. The FID is an excellent detector (Appendix B) for this type of measurement because the response is nearly constant per carbon atom and the dynamic range is wide.

Regulators have separated the Modified 8015 into two methods: one for the analysis of gasoline-type products and one for the analysis of diesel-type products. Purge and trap is used for introducing samples for analysis of gasolinelike products, whereas samples containing higher-boiling-point petroleum products are usually extracted, followed by direct injection into the GC.
APPENDIX E

X-RAY FLUORESCENCE ANALYSIS
X-RAY FLUORESCENCE ANALYSIS

The traditional approaches for metal analysis are flame and graphite furnace atomic absorption and inductively coupled plasma–atomic emission spectroscopy. As described in Appendix C, these methods provide accurate, precise, and specific measurements of solution concentrations in the parts per billion (ppb) range and lower. Thus, they are an integral part of the Contract Laboratory Program (CLP) at hazardous waste sites. Metal contamination of soils is a major environmental problem. Lead is found at elevated levels at about 30% of Superfund sites; arsenic, cadmium, chromium, and zinc are each found at about 15% of the sites.

At a typical contamination site, the investigative team needs to collect, analyze, and map soil samples. When an outside laboratory is used for the chemical analyses, there is often a delay of several weeks between sample submission and analysis results. After the first round of results are reviewed, it is often necessary to remobilize crews to the site for additional samples and mapping. The costs of the CLP analyses ($200 or more per sample) and the added expense of sampling, (re)mobilization, and site mapping incurs formidable expense.

Part of the high cost of CLP analysis can be attributed to the substantial sample manipulation required prior to actual measurement. As described in Section 3, such manipulations include digestions, filtering, dissolutions, and dilutions. X-ray fluorescence (XRF) is promising, particularly for screening soil samples, as an alternative to detailed CLP analyses. X-ray fluorescence has the following advantages:

- Measurements are made directly on the soil samples, not on solutions. Sample preparation, even in the most stringent cases, is not very demanding.
- Measurement times take place in seconds, making sample cycle times short.
- XRF is applicable to all but the very lightest (low atomic number) elements.
- The dynamic range overlaps with that of typical soil contamination (ppm to 100%).

Field-portable XRF has been used for many years as a tool in the mining industry to detect metals. In recent years, several instrumental advances have made its application to environmental and hazardous waste site investigations feasible. XRF can be used in a field-screening mode to locate and identify potential sources of contamination, to define the extent of contamination, to document the attainment of cleanup goals, and to determine cleanup and disposal options. Especially encouraging is the indication that field mobile analytical quality instruments can provide quantitative analysis results of comparable accuracy to those obtained using the standard and slower CLP methodology.

Basis of the Technique. In common with the other spectroscopic methods described in Appendix C, XRF is compatible with both qualitative and quantitative analysis. When materials are bombarded with primary x-rays, they emit secondary x-rays that are characteristic of the elements contained in the sample. The efficiency of secondary x-ray generation for a given element is a
function of the primary excitation conditions. Since XRF results from many different elements using the same source, a means is necessary to resolve the photon energies (wavelengths) of the secondary x-rays. The technique is therefore more precisely described as energy-dispersive x-ray fluorescence (EDXRF) analysis. The intensities of the resolved peaks, when compared with those of suitable standards, provide the quantitative analytical data. An example of an x-ray spectrum of a contaminated soil showing the clearly delineated metal emission lines is given in Figure 1.

X-RAY SOURCES AND DETECTORS

There are distinct options for the source and detector choices in XRF. The most versatile sources and those that give the best detection limits are conventional x-ray tubes that can be operated up to 50 kV. By automatic selection of voltage and current settings and primary radiation filters an instrument's sensitivity can be optimized in the low, medium, or high $Z$ ($Z =$ atomic number) ranges.

The alternative radioisotopic sources are much lighter and less expensive, making them useful for portable analyzers and field-screening applications. However, they lead to higher limits of detection, owing to their lower output intensities. In order to analyze a range of elements, the operator must physically remove one source and repeatedly replace it with another. Some typical radioisotopic source data are shown in Table 1.

![X-ray spectrum of contaminated soil showing metal emission lines](image)

Figure 1. The peaks shown are representative of metal species in contaminated soil. The signal intensity is a measure of the amount of metal present.
TABLE 1

Radioisotopic Sources for Field XRF

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half-Life</th>
<th>Emission</th>
<th>K-Lines</th>
<th>L-Lines</th>
<th>Detector</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-55</td>
<td>2.7 years</td>
<td>Mn K x-rays</td>
<td>Si–V</td>
<td>Nb–Ce</td>
<td>Ne</td>
</tr>
<tr>
<td>Cm-244</td>
<td>17.8 years</td>
<td>Pu L x-rays</td>
<td>Ti–Se</td>
<td>La–Pb</td>
<td>Ar</td>
</tr>
<tr>
<td>Cd-109</td>
<td>1.3 years</td>
<td>Ag K x-rays</td>
<td>Cr–Mo</td>
<td>Tb–U</td>
<td>Ar</td>
</tr>
<tr>
<td>Am-241</td>
<td>433 years</td>
<td>59.6 keV gamma rays</td>
<td>Zn–Nd</td>
<td>Hf–U</td>
<td>Ar</td>
</tr>
</tbody>
</table>

Three different isotope sources are needed to cover the entire element range. Generally the K-lines are preferred. The working life of the Fe-55 and Cd-109 sources is about 4 years each.

Detectors. The same performance, price, and convenience trade-offs found with x-ray sources also apply to detectors. Field screening units generally incorporate gas-filled proportional counters. They are rugged and lightweight; however, their resolution can pose problems in separating the fluorescence lines of different elements that are both present in appreciable amounts. Lead and arsenic are a classical overlapping combination.

The laboratory EDXRF unit employs a liquid nitrogen (LN) cooled solid-state lithium-drifted Si(Li) detector, which offers much higher resolution than the proportional counters. Although overlaps are not completely eliminated, the characteristic emission lines of different elements are sufficiently separated that qualitative analysis is possible by visual inspection of the spectra (Figure 2). Improved resolution also contributes to more sensitive and precise quantitative analysis. Unfortunately, such units tend to be bulky and not easily mobilized. However the Peltier thermoelectrically cooled Si(Li) detector does not require LN-cooling and gives typical resolution of 185 eV, only slightly wider than the 155 eV for LN-cooled Si(Li) detectors. This has led to a new category of instruments called field-mobile analytical quality EDXRF. This detector has been installed and used for various applications over the past two years and has shown a high degree of reliability, stability, and durability. Another development of note is an experimental field-portable LN-cooled detector with a hold time of up to 8 hours.

SAMPLE COLLECTION AND PREPARATION

As noted above, sample preparation for EDXRF analysis requires considerably less time than a CLP digestion. The degree of sample preparation depends on the data quality objectives (DQOs). Sample preparation can be as simple as collecting soil in a sample cup, although usually the sample is dried, sieved, and pulverized before analysis to improve accuracy and precision.

In Situ Analysis. In situ analysis is made with the probe of a hand-held field-portable instrument literally pressed against the ground. The x-rays penetrate only 2 or 3 millimeters into the soil. Because only surface levels of contamination are assessed, hot spots can be completely covered with as little as 0.4 cm of soil. All surface debris should be removed from the chosen sampling location. Cross-
contamination of the probe is avoided by placing a single-thickness plastic sample bag or polypropylene film over the probe. The probe is pressed firmly to the ground to maximize its contact with the ground surface.

In situ measurements can exhibit a high degree of variability owing to the natural heterogeneity of the soil. Averaging of multiple readings helps to minimize this effect. For example, in a 1-foot-square area, three readings can be taken in a triangular pattern. Or in a 3-foot by 3-foot area, five readings can be taken, one at each vertex of the square and one in the center, and averaged. XRF results may not be representative if single measurements are used at one sample location. Minimum measurement time is 30 seconds. All samples should be measured for the same period of time, and all readings should be recorded.

Field-portable XRF units cannot analyze for elements with lower atomic weights than chromium. There can be interferences from overlapping x-ray lines of two different elements such as lead and arsenic. Sample moisture is a potential interferent, especially at levels above 20%. It is a major source of error in saturated soils.

Discrete Samples XRF Analysis. The inhomogeneous and surface-specific complications of in situ analysis can be greatly reduced at the expense of a more involved and longer analysis. Discrete samples are collected and subjected to some type of field preparation prior to analysis. Surface and shallow soil samples can be collected by hand with trowels or augers. Drill rigs or direct push samplers allow for deeper subsurface sampling. The EPA recommends that a minimum of 100–200 g of sample be delivered for analysis. One approach is to mix 1-kg samples and then subsample.
The simpler version of discrete XRF sampling involves collection of samples in plastic bags, rough-sieving to remove organic debris and rocks, and homogenization by mixing directly in the bag. The XRF readings are then taken directly through the bag. Three measurements are taken on each bag, which is shaken between measurements. Measurement times of 30–50 seconds are recommended. Following the completion of the XRF measurements, a minimum of 10% of the samples should be sent for confirmation analysis by AA/ICP. Typically the sample is split in half, with one half going for laboratory analysis and the other half archived. Note that the necessity for confirmation analysis in the laboratory is not eliminated.

The second method of sample preparation is more rigorous. The sample is dried, either by air in a conventional oven at 105°C, a microwave oven, or with a moisture balance. Appropriate caution should be taken for drying with microwave or conventional ovens if lead, mercury, or arsenic is known or suspected to be present in the samples. After the sample has been dried, foreign objects such as twigs, leaves, grass, and pebbles are removed, agglomerates and lumps are broken up, but not ground, and the material is sieved with a 10- or 20-mesh sieve; the coarse factor is discarded.

The sieved contents are placed in a cup and settled by tapping to create a reasonably smooth and uniform surface. The sample is then covered with mylar film and analyzed for 50 seconds. The cup is shaken and reanalyzed twice more for a total of three readings, which are averaged. The prepared sample cups are saved and at least 10% of them are sent for confirmed analysis by AA/ICP. A variation of the above technique involves splitting the sample after sieving and grinding about 10 g with a mortar and pestle or grinder. If the soils are ground mechanically, all samples should be ground under the same conditions to a recommended 100 mesh. The purpose is to improve the homogeneity of the surface presented to the X-ray probe.

Performance. The Spectrace 6000 EDXRF system uses the high-resolution Peltier-cooled detector and is easily installed in an on-site laboratory van for movement to a contamination site. It is rugged enough so that vibration from transportation does not affect calibration. It is composed of three basic modules: the spectrometer containing the x-ray tube detector and sample chamber, a card cage housing the electronics, and a personal computer. Using an automated 50-kV x-ray source with a selection of primary radiation filters, this EDXRF system provides the low-ppm detection limits required for on-site field screening. Table 2 lists lower limits of detection (LLDs) and quoted values for field-portable units of metals in soil.

Although not included in the table, the other metals of interest to the gas industry (aluminum, barium, cobalt, magnesium, mercury, selenium, sodium, thallium, vanadium) are also detectable.
### TABLE 2

<table>
<thead>
<tr>
<th>Element</th>
<th>Field-Mobile Analytical Quality</th>
<th>Analytical Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony</td>
<td>5</td>
<td>100–200</td>
</tr>
<tr>
<td>Arsenic</td>
<td>8</td>
<td>100–200</td>
</tr>
<tr>
<td>Cadmium</td>
<td>4</td>
<td>100–200</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.02%</td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td>16</td>
<td>300–500</td>
</tr>
<tr>
<td>Copper</td>
<td>16</td>
<td>200–400</td>
</tr>
<tr>
<td>Iron</td>
<td>19</td>
<td>100–200</td>
</tr>
<tr>
<td>Lead</td>
<td>6</td>
<td>100–200</td>
</tr>
<tr>
<td>Manganese</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>14</td>
<td>150–250</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.03%</td>
<td></td>
</tr>
<tr>
<td>Silver</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Tin</td>
<td></td>
<td>100–200</td>
</tr>
<tr>
<td>Zinc</td>
<td>11</td>
<td>150–300</td>
</tr>
</tbody>
</table>
APPENDIX F

ELECTROCHEMISTRY
ELECTROCHEMISTRY

Analytes can be caused to interact quantitatively with electrical potentials and currents. Methods utilizing electrical stimuli for chemical analysis are termed electroanalytical methods. Electrochemical investigations involve the measurement of one or more of the following parameters: potential (E, volts), current (i, amps) and time (t, secs). Electrochemical techniques are based on the formation of a circuit in which an anode (loss of electrons) and cathode (gain of electrons) pair form the basis of the electrochemical potential and current sources. A brief introduction of the general methods is given. However, only those methods with importance in environmental analysis will be elaborated on in greater detail.

Electrogravimetry. Many different metal cations can be reduced quantitatively to the metal at the cathode of an electrolytic cell. The deposited material is weighed and used to calculate the amount of cation. The choice of applied deposition potential depends on the analyte of interest and the overpotential — the potential relative to a given reference electrode at which the free element will lose an electron (become oxidized). The deposition can be carried out at constant current or constant potential. With the application of the proper voltage difference and experimental conditions, co-deposition is avoided. With proper choice of a series of potentials applied to the cathode, many cations can be quantitated in a single experiment.

Conductimetry. When an external potential difference is applied to a solution, the ions in the solution are responsible for conduction of current through the solution. The solution conductivity is a measure of the concentration of ions. For solutions of a single ionic substance, the concentrations can be calculated from the measured conductivity. However, the current carrying ability varies from one ion to another. Thus, the conductivity of a mixture is not readily converted to a concentration.

The implementation of conductimetry requires the application of a voltage difference in the AC mode (1000 Hz). This inevitably creates a capacitance, in addition to the resistance of the solution. Sophisticated electronics in modern apparatus has alleviated this problem for instruments operated at moderate AC frequencies.

Coulometry. Coulometry exploits Faraday's laws of electrolysis, similar to electrogravimetry, but in a more general sense. The analyte in its entirety is made to undergo an electrochemical transformation. Examples include the reduction of a metal cation (primary process) to the metal, and the conversion of chloride to silver chloride with a silver electrode (secondary process). The mass of a substance produced, W, at an electrode is related to the quantity of current passed through the solution by

\[ W = \frac{MQ}{95487n} \]

where M is the atom/molecular molar mass of the deposited substance, n is the number of electrons associated with the deposition, and Q is the total charge passed during the deposition. The quantity Q is directly measured in coulometry. Both constant potential or constant current conditions are possible for coulometric analysis, but in either case the current efficiency must be close to 100%. In the
constant potential mode, the current is integrated over time by a coulometer, which gives very accurate values for Q. Note that coulometry does not require standards for determinations.

POTENTIOMETRY (ION-SELECTIVE ELECTRODES)

Potentiometry refers to the measurement of electrode potential, which is related to concentrations of species participating in joint oxidation (loss of electrons) and reduction (gain of electrons) processes. The electrode involving the reduction/oxidation (redox) species of the analyte is referred to as the indicator electrode or test electrode. There are many different kinds of electrodes available, but we will focus on only a limited number here.

The electrode potential of a single electrode cannot be measured. The measurable quantity is a potential difference between electrodes in an electrochemical cell. Thus, the potential of a ‘test electrode’ is measured by coupling it with a standard reference electrode. The standard reference electrodes commonly used are the calomel and silver/silver chloride electrodes.

An ion-selective electrode (ISE) is designed to respond to a particular ion. ISEs, also referred to as indicator electrodes, are actually half-cells composing one-half of a battery. The familiar pH electrodes are ISEs that respond to hydrogen ion concentration. The dependence of the electrode potential on concentration allows it to directly measure the amount of ions or species of interest. ISEs come in two configurations; either as single electrodes (half cell) or combination electrodes. Combination electrodes are actually a complete electrochemical cell made up of the indicator/sensing electrode and a reference electrode. In the other configuration, an external reference electrode must be coupled to set up the electrochemical cell.

There are many types of ISEs. The pH electrode is a glass membrane electrode as are sodium-, silver-, and potassium-sensing electrodes. The potential developed at a glass membrane is measured is are often affected by other undesirable ions. Membranes other than the glass membranes have been developed. Inorganic salts can be sealed in polymers, whereby ion-exchange processes lead to development of a potential. These solid-state electrodes have been used with membranes to make halide ion-sensing electrodes. Gas-sensing electrodes use gas-permeable membranes and pH electrodes in combination to sense carbon dioxide and sulfur dioxide. Polymer membrane electrodes are made of ion-exchange materials in a polymer matrix.

The cell potential \(E\) depends strongly on the ionic strength of the solutions being measured. Use of ionic strength adjusters is therefore a common practice. Standardization is highly recommended whenever ISEs are used. A common error inherent to ISEs is the "sodium ion error," due to the fact that ISEs are never completely specific for one type of ion and that sodium happens to be a major interferent (especially for glass electrodes). Temperature control is a must when working with ISEs. Static electricity can lead to erroneous readings. Aging of the electrodes and high variations in pH changes the ideal response of the electrode. Availability of microprocessor-controlled ion meters provides temperature compensation, automatic standardization, and correct compensation for nonideal response for pH temperature changes.
Table 1 is a description of several commonly used, commercially available ISEs. The name of the electrode corresponds to the material from which the electrode is constructed and hence the kind of analyte or species to be measured.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Type</th>
<th>Range, ppm</th>
<th>Response, seconds</th>
<th>Time Sensitivity, mV/decade</th>
<th>Interferences</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>Gas sensing</td>
<td>0.008–17000</td>
<td>20</td>
<td>-58</td>
<td>Volatile amines</td>
</tr>
<tr>
<td>Bromide</td>
<td>Solid state</td>
<td>0.04–79900</td>
<td>20</td>
<td>-56</td>
<td>I-,CN-,S2-</td>
</tr>
<tr>
<td>Calcium</td>
<td>Solid state</td>
<td>0.201–40100</td>
<td>25</td>
<td>+28</td>
<td>None</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>Gas sensing</td>
<td>0.440–1320</td>
<td>35</td>
<td>+56</td>
<td>Volatile organic acids</td>
</tr>
<tr>
<td>Chloride</td>
<td>Solid state</td>
<td>0.178–35500</td>
<td>20</td>
<td>-57</td>
<td>Br-,I-,CN-,S2-, OH</td>
</tr>
<tr>
<td>Copper(II)</td>
<td>Solid state</td>
<td>0.032–63500</td>
<td>20</td>
<td>+27</td>
<td>S2-, Ag+, Hg2+, Fe3+, Cd2+</td>
</tr>
<tr>
<td>Cyanide</td>
<td>Solid state</td>
<td>0.013–260</td>
<td>20</td>
<td>-63</td>
<td>I-, S2-</td>
</tr>
<tr>
<td>Divalent Cation</td>
<td>Solid state</td>
<td>0.080–40000</td>
<td>25</td>
<td>+27</td>
<td>Na+</td>
</tr>
<tr>
<td>Fluoride</td>
<td>Solid state</td>
<td>0.0095–19000</td>
<td>&lt;20</td>
<td>+59</td>
<td>Metal ions, pH&lt;5, pH&gt;10</td>
</tr>
<tr>
<td>Iodide</td>
<td>Solid state</td>
<td>0.635–127000</td>
<td>20</td>
<td>-59</td>
<td>CN-, S2-</td>
</tr>
<tr>
<td>Lead</td>
<td>Solid state</td>
<td>0.207–207000</td>
<td>25</td>
<td>+27</td>
<td>Fe3+, Hg2+, Ag+, S2-</td>
</tr>
<tr>
<td>Nitrate</td>
<td>Solid state</td>
<td>0.310–310000</td>
<td>25</td>
<td>-57</td>
<td>Cl-,ClO4-, I-, Br</td>
</tr>
<tr>
<td>Nitrite</td>
<td>Gas sensing</td>
<td>0.002–920</td>
<td>30</td>
<td>+58</td>
<td>Volatile organic acids</td>
</tr>
<tr>
<td>Silver/Sulfide</td>
<td>Solid state</td>
<td>0.011–107900</td>
<td>20</td>
<td>+59</td>
<td>Hg2+</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.016–32100</td>
<td></td>
<td>-27</td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>Glass</td>
<td>0.023–saturation</td>
<td>&lt;90</td>
<td>+57</td>
<td>High-level cations</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>Gas sensing</td>
<td>0.064–640 ppm</td>
<td>&lt;30</td>
<td>+55</td>
<td>Volatile organic acids, CO2, NO2</td>
</tr>
</tbody>
</table>
VOLTAMETRY (ANODIC STRIPPING VOLTAMMETRY)

An important voltametric technique includes anodic stripping voltametry (ASV). In voltametry, the current at a working electrode is measured as a function of a systematically varying potential. The resulting current potential curve, known as a voltamogram, is analyzed for qualitative and quantitative information concerning the electroactive analytes. Changes in potential at the electrode surface are indicative of oxidation or reduction of the electroactive species. These changes in potentials are species-specific, and the amount of current produced is proportional to the amount of analyte present. Therefore, this technique can be qualitative and quantitative in its detection. All voltammetric experiments are done in deoxygenated solutions.

Anodic stripping voltametry is a two-step process. First, analytes are deposited by reduction via a deposition potential more negative (usually −1 volt) than the reduction potentials of all the analytes. The deposition step can last several minutes. The electrode is a microelectrode (0.3 to 20 μm). After a "rest" time, the potential is then linearly ramped to more positive values to oxidize (redissolve) the deposited analytes. As the potential is changed, the current is monitored to track oxidation of the analytes of interest as they are redissolved into the solution to form cationic species. Figure 1(a) depicts the course of the voltage settings for deposition and stripping. Part (b) illustrates the current response caused by the oxidation of the analytes as they reach their respective reduction potentials. The potential at which oxidation occurs and the oxidation amount of current provide information about the analytes and their concentration.

Thin mercury films (TFME) and static mercury drops are commonly used as working electrodes in ASV. Thin films serve as efficient media for the deposition or absorption of analytes prior to reduction. The shorter average diffusion pathlength for species embedded in thin films, compared to species embedded in mercury drops, allows for faster escape of the analyte upon voltage ramping. This results in narrow and larger voltametric peaks, which represent higher sensitivity and better resolution of analytes in mixtures. Unfortunately, there is less precision with the thin-film method as opposed to the hanging mercury drop technique. Determination of analyte species in the range from $10^{-6}$ to $10^{-9}$ M (molar mass) are readily feasible and rapidly performed with this technique.
Figure 1. (a) Potential signal for a stripping measurement for Cd$^{2+}$ and Cu$^{2+}$.

(b) The corresponding stripping voltammogram for the process in (a).
APPENDIX G

IMMUNOASSAY TEST KITS
IMMUNOASSAY TEST KITS

Immunoassay field-screening methodology has developed rapidly in the past several years and represents an unconventional approach to contaminant detection. Unlike other physical methods, the immunoassay technology is based on traditional clinical/biological chemistry techniques, which exploit an immune system's ability to produce antibodies in response to foreign molecules. Although these methods are gaining widespread attention among environmental testing firms, their maturity and measure of reliability are still being considered.

Immunoassay test kits are available for several classes of petroleum hydrocarbons (including BTEX and PAHs), mercury, and pesticide contaminants. Immunoassay tests are claimed to be ideal for field screening owing to the following combination of attributes:

- Analyte specificity
- Ease of use
- Low cost and rapid time response (<30 minutes)
- Insensitivity to variations in temperature, humidity, or volatility of analytes
- Accuracy and precision of measurements
- Compatibility with complex matrices and in the presence of other compounds

While some of these claims are exaggerated, the value of immunoassay test kits has been unquestionably established. A field analytical method for petroleum hydrocarbons based on commercially available immunoassay technology has received approval for inclusion in the third update of the EPA Office of Solid Waste's methods manual.

Immunoassay tests rely on the affinity between an antigen and an antibody. Briefly, an antigen is a region on a foreign body or molecular moiety that can be recognized by an active site of an antibody. Recent progress in immunology and biotechnology, particularly monoclonal antibody techniques, has made it possible to produce a wide range of pure antibodies against almost any antigen. The binding of an antigen (foreign molecule) to an antibody occurs by the formation of multiple noncovalent bonds. The specificity of the binding arises because the shape of the antibody-active site "fits" the antigen determinant so that significant binding forces hold the antibody and antigen complex together. Antigen–antibody binding follows a dynamic equilibrium relationship in which the concentrations of free antigen, free antibody, and antigen–antibody complex become constant with time. The higher the equilibrium constant, the stronger the antigen binds to the antibody.

The three approaches to the immunoassay method include radioimmunoassay (RIA), enzyme immunoassay (EIA), and the fluorescent and chemiluminescent label method. EIA and RIA are popular techniques, although fluorescent and chemiluminiscent techniques are gaining greater attention. Radioimmunoassays function by competitively binding 30% to 50% of a radioactive tracer to the antibody hosts. The tracer is typically a radioactive analyte, composed of $^3$H or $^{125}$I atoms, which has preferentially less affinity for the antibody than does the analyte of interest. This is undertaken in the absence of the analyte of interest. Partial displacement of the radioactive tracer after
the addition of the analyte and the establishment of equilibrium results in a corresponding decrease in measured radioactivity from the immunoassay antibody medium. The corresponding degree of radioactivity serves as a measure of the bound analyte. Calibration curves are used to correlate the radioactivity with an actual analyte concentration.

An alternative to RIA detection is EIA, which uses enzyme activity as a replacement for the radioactive tracers of RIA. EIA detection has proven to be safer, more versatile, and more easily applied to field use. It has also proven to be as sensitive and more cost-effective than many of the RIA methods. EIA methods, which use fluorometric detection to measure enzyme activity, have detected analytes down to levels of $10^{-18}$ to $10^{-21}$ M.

EIA methods are based on the competitive binding of the antigen to the binding of an enzyme-tagged derivative of the analyte (enzyme conjugate). Higher concentrations of antigen result in a greater number of binding sites on the antibody. Thus, by determination of the fraction of antibody binding sites that are occupied by the antigen, the concentration of the antigen in the test solution can be determined. A calibration curve is required to make clear the relationship between concentration and measured response. From a practical standpoint, it is easier to measure the binding of the enzyme conjugate than the binding of the antigen itself. An inverse relationship exists between the developed color and antigen concentration in the test solution.

The difficulties associated with EIAs tend to lie in the precision of the results. End-point measurements are difficult to determine, and the presence of an additional step in the assay development affects the overall precision of the testing. Immunoassay methods are not highly quantitative in general. Absorbance is measured (Appendix C), which is linearly related to concentration via Beer's Law. In immunoassay, the color scales vary linearly with the logarithm of the

![Figure 1. The peaks shown are representative of metal species in contaminated soil. The signal intensity is a measure of the amount of metal present.](image-url)
concentration of the target analyte. Uncertainties of the measured absorbencies result in a corresponding degree of uncertainty in the concentration. To counteract the problem, different immunoassay preparations designed to cover a relatively narrow concentration range can be used. The user is able to specify whether the concentration is above or below a certain action level. Since immunoassays are essentially a biological activity, moderate temperature changes can adversely affect the nature of the binding, which results in reduced immunoassay activity. Currently, both EIA and RIA are considered equally valid, although EIAs are more susceptible to interferents than RIA methods.

A defining characteristic of immunoassay methods is the specificity of the binding between the analyte and the antibodies, for example, the pesticide antibodies do not detect petroleum hydrocarbons. Within the class of petroleum hydrocarbons, there are many different individual compounds, and the distribution can vary widely from one site to another. Weathering and other phenomena can also cause variations. In the case of PAHs, the relative response covers more than two orders of magnitude. An example used to demonstrate this range is taken from the Field Screening Methods for Hazardous Wastes and Toxic Chemicals. Table 1 is a list of the cross-reactivity of many PAH species reported from the PAH RES test kit. Whenever possible, it is best to use standards as close as possible in chemical composition to the analytes present in actual test samples. For example, naphthalene gives only about 0.5% of the response of phenanthrene or anthracene.

### TABLE 1

Cross-Reactivity of PAH Species Using Immunoassay Detection

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ring Number</th>
<th>Concentration Giving a Positive Result with PAH RISC Test Kit ppm</th>
<th>% Cross-Reactivity Compared to Phenanthrene, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenanthrene</td>
<td>3</td>
<td>1.0</td>
<td>100</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>2</td>
<td>200</td>
<td>0.5</td>
</tr>
<tr>
<td>Anthracene</td>
<td>3</td>
<td>0.81</td>
<td>123</td>
</tr>
<tr>
<td>Fluorene</td>
<td>3</td>
<td>1.5</td>
<td>67</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>3</td>
<td>7.5</td>
<td>13</td>
</tr>
<tr>
<td>Chrysene</td>
<td>4</td>
<td>1.2</td>
<td>84</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>4</td>
<td>1.4</td>
<td>73</td>
</tr>
<tr>
<td>Benzo[a] anthracene</td>
<td>4</td>
<td>1.6</td>
<td>64</td>
</tr>
<tr>
<td>Pyrene</td>
<td>4</td>
<td>3.5</td>
<td>29</td>
</tr>
<tr>
<td>Benzo[b] fluoranthene</td>
<td>5</td>
<td>4.6</td>
<td>22</td>
</tr>
<tr>
<td>Benzo[a] pyrene</td>
<td>5</td>
<td>8.3</td>
<td>12</td>
</tr>
<tr>
<td>Benzo[k] fluoranthene</td>
<td>5</td>
<td>9.4</td>
<td>11</td>
</tr>
<tr>
<td>Dibenzo[a,h] anthracene</td>
<td>5</td>
<td>&gt; 200</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>Indeno[1,2,3-cd] pyrene</td>
<td>6</td>
<td>11</td>
<td>9.4</td>
</tr>
<tr>
<td>Benzo[ghi] perylene</td>
<td>6</td>
<td>&gt; 200</td>
<td>&lt; 0.5</td>
</tr>
</tbody>
</table>
APPENDIX H

SUPPLEMENTARY REFERENCES AND FURTHER RESOURCES
SUPPLEMENTARY REFERENCES AND FURTHER RESOURCES


EPA/AWMA Field Screening Methods Conference, 1993, Las Vegas, NV.


