United States
Environmental Protection
Agency

Research and Development

Environmental Monitoring Systems
Laboratory
Las Vegas NV 89114

EPA-600/S4-83-040 Jan. 1984

EPA

Project Summary

Characterization of Hazardous Waste Sites - A Methods Manual, Volume II, Available Sampling Methods

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This volume is a compilation of methods and materials suitable to address most needs that arise during routine waste site and hazardous spill investigations. It is part of a multivolume manual developed by the U.S. Environmental Protection Agency to serve a wide variety of users as a source of information, methods, materials and references on the subject. This volume is organized by media. After a first introductory chapter on general problems, the second chapter addresses solids and provides eight detailed instructions on sampling methods for soils, sludges and sediments, and bulk materials. Chapter Three addresses liquids. Ten methods are detailed for surface waters, containerized liquids, and groundwater. Gases, vapors, and aerosols are covered in Chapter Four. Twelve methods are presented for ambient air, soil gases and vapors, and headspace gases. The last chapter briefly discusses ionizing radiation survey instruments. Every method is referenced, and a large bibliography is provided. Appendices are included to make the volume a useful field manual. They cover Sample Containerization and Preservation, Equipment Availability and Fabrication, Packing and Shipping Guidelines, Document Control and Chain-of-Custody Procedures, and Applicable Tables (of statistics and conversion factors). This volume will be revised annually.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Investigations at hazardous waste and environment-threatening spill sites place more restrictive demands on personnel, materials and methodologies than those usually found in routine environmental surveys. As a result, traditional procedures and protocols used for the acquisition of environmental samples often fail to meet the rigors and demands required for many hazardous waste sampling applications. Thus, the collection of hazardous waste samples will frequently require specialized equipment and protocols either developed specifically for such uses or modified from preexisting materials and/or techniques. Some important considerations are:

- Methods and materials must be suitable to a wide range of situations and applications because of the unknown nature of many hazardous waste investigations and environmental spill responses.
- Hazardous wastes, by definition, are associated with both acute and chronic exposure to dangerous, toxic chemicals and this dictates that expeditious sample collection methods be used to minimize personnel exposure.
- Because of the nature of the materials being sampled, the option of using disposable sampling

equipment must be considered because attempting cleanup efforts in the field can be impractical.
- Hazardous waste site investigations and response actions at environment-threatening spills generally require some level of hazard protection that may be cumbersome, limit the field of vision, or fatigue the sampler. Sample collection procedures must therefore be relatively simple to follow to expedite sample procurement and to reduce the chance of fatigue. Collection and monitoring equipment should be simple to operate, direct reading, and should not be unwieldy.

These and other factors associated with the procurement of hazardous waste samples need to be addressed in a compilation of practical, cost effective, and reliable methods and procedures capable of yielding representative samples for a diverse number of potential parameters and chemical matrices. These methods must be consonant with a variety of analytical considerations running the gamut from gross compatibility analyses (pH, flammability, water reactivity, etc.) to highly sophisticated techniques capable of resolution in the part per billion (ppb) range.

Method Selection Criteria

Even a limited literature survey will disclose the existence of a great number of sampling methods, all of which have certain merits that warrant consideration. Therefore, selection criteria were chosen on which to base decisions for including the sampling methods found in this manual. The following is a listing, not necessarily in order of relative importance, of these criteria:

- Practicality
- Representativeness
- Economics
- Simplicity or Ease of Operation
- Compatibility with Analytical Considerations
- Versatility
- Safety

Purpose and Objectives of Sampling

The basic objective of any sampling program is to produce a set of samples representative of the source under investigation and suitable for subsequent analysis. More specifically, the objective of sampling hazardous wastes is to acquire information that will assist investigators in identifying unknown compounds present and to assess the extent to which these compounds have become integrated into the surrounding environment. Subsequently, this acquired information may be used in future litigations as well as to assist investigators in the development of remedial actions.

The term "sample" can most simply be defined as a representative part of the object to be analyzed. This definition needs to be qualified further, however, by the consideration of several criteria.

Of utmost importance is representativeness. To meet the requirement of representativeness, the sample needs to be chosen so that it possesses the same qualities or properties as the material under consideration. However, the sample needs only resemble the material to the degree determined by the desired qualities under investigation and the analytical techniques used.

Sample size is also an important criterion to be considered. Sample size must be carefully chosen with respect to the physical properties of the entire object and the requirements and/or limitations of the analytical procedure. For example, although the entire contents of an intact 55-gallon drum can certainly be considered a representative sample of the drum material, it is an impractical sample because of its bulk. Alternatively, too small a sample size can be just as limiting, since representativeness and analytical volume requirements might be jeopardized.

A third criterion for consideration is maintenance of sample integrity. The sample must retain the properties of the parent object (at the time of sampling) through collection, transport, and delivery to the analyst. Degradation or alteration of the sample through exposure to air, excess heat or cold, microorganisms, or to contaminants from the container must be avoided.

Finally, the number and/or the frequency of subsamples (e.g., samples making up a composite) required and the distribution of these subsamples need to be considered.These criteria are often dictated by the nature of the material being sampled; that is, whether the material is homogeneous or heterogeneous. For example, if a material is known to be homogeneous, a single sample may suffice to define its quality. However, if a sample is heterogeneous, a number of samples collected at specified time intervals or distances may be necessary to define the characteristics of the subject materials. In addition, the nature of the chemical parameters to be identified and the way the analytical results will be used are also important when the number and/or frequency of the samples to be collected are determined.

Types of Samples

Before defining the general sample types, the nature of the object or materials under investigation must be discussed. Materials can be divided into three basic groups as outlined in Figure 1.

Of least concern to the sampler are homogeneous materials. These materials are generally defined as having uniform composition throughout. In this case, any sample increment can be considered representative of the material. On the other hand, heterogeneous samples present problems to the sampler because of changes in the quality of the material over distance.

When discussing types of samples, it is important to distinguish between the type of media to be sampled and the sampling technique that yields a specific type of sample. In relation to the media to be sampled, two basic types of samples can be considered: the environmental sample and the hazardous sample.

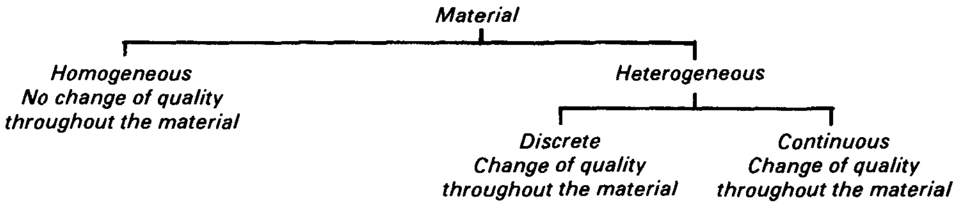
Environmental samples (ambient air, soils, rivers, streams, or biota) are generally dilute (in terms of pollutant concentration) and usually do not require the special handling procedures used for concentrated wastes. However, in certain instances, environmental samples can contain elevated concentrations of pollutants and in such cases would have to be handled as hazardous samples.

Hazardous or concentrated samples are those collected from drums, tanks, lagoons, pits, waste piles, fresh spills, etc., and require special handling procedures because of their potential toxicity or hazard. These samples can be further subdivided based on their degree of hazard; however, care should be taken when handling and shipping any wastes believed to be concentrated, regardless of the degree.

In general, two basic types of sampling techniques are recognized, both of which can be used for either environmental or concentrated samples.

Grab Samples

A grab sample is defined as a discrete aliquot representative of a specific location at a given point in time. The sample is collected all at once and at one particular point in the sample medium. The representativeness of such samples is defined by the nature of the materials being sampled. In general, as sources vary over time and distance, the repre-



Homogeneous	*Discrete Changes*	*Continuous Changes*
Well-mixed liquids	*Ore pellets*	*Fluids or gases with gradients*
Well-mixed gases	*Tablets*	*Mixture of reacting compounds*
Pure metals	*Crystallized rocks*	*Granulated materials with granules much smaller than sample size*
	Suspensions	

Figure 1. *Types of material*

sentativeness of grab samples will decrease.

Composite Samples

Composites are nondiscrete samples composed of more than one specific aliquot collected at various sampling locations and/or different points in time. Analysis of this type of sample produces an average value and can in certain instances be used as an alternative to analyzing a number of individual grab samples and calculating an average value. It should be noted, however, that compositing can mask problems by diluting isolated concentrations of some hazardous compounds below detection limits.

For sampling situations involving hazardous wastes, grab sampling techniques are generally preferred because grab sampling minimizes the amount of time sampling personnel must be in contact with the wastes, reduces risks associated with compositing unknowns, and eliminates chemical changes that might occur due to compositing. Compositing is still often used for environmental samples and may be used for hazardous samples under certain conditions. For example, compositing of hazardous waste is often performed (after compatibility tests have been completed) to determine an average value over a number of different locations (group of drums). This procedure provides data that can be useful by providing an average concentration within a number of units, can serve to keep analytical costs down and can provide information useful to transporters and waste disposal operations.

Sampling Plan

Before any sampling activities are begun, it is imperative that the purpose and goals of a program and the equipment, methodologies, and logistics to be used during the actual sampling be identified in the form of a work or sampling plan. This plan is developed when it becomes evident that a field investigation is necessary and should be initiated in conjunction with or immediately following the preliminary assessment. This plan should be clear and concise and should detail the following basic components:

- background information collected during the preliminary assessment;
- objectives and goals of the investigation;
- sampling methods to be used, including equipment needs, procedures, sample containment, and preservation;
- justification for selected methods and procedures;
- sample locations, as well as, number and types of samples to be collected at each;
- organization of the investigative team;
- safety plan (includes safety equipment and decontamination procedures, etc.);
- transportation and shipping information;
- training information; and
- additional site-specific information or requirements.

Note that this list of sampling plan components is by no means all inclusive and that additional elements may be added or altered depending on the specific requirements of the field investigation. It should also be recognized that although a detailed sampling plan is quite important, it may be an impractical undertaking in some instances. Emergency responses to accidental spills would be a prime example of such an instance where time might prohibit the development of a site-specific sampling plan. In such a case, the investigator would have to rely on general guidelines and personal judgment, and the sampling or response plan might be simply a strategy based on preliminary information and finalized on site. In any event, a plan of action needs to be developed, no matter how concise or informal, to aid investigators in maintaining a logical and consistent order to the implementation of their task. Planning and safety are discussed in detail in Volumes I, IV and V.

Sampling Schemes

The manner in which samples are selected generally falls into one of (or a combination of) the following categories.

Random Sampling

Random sampling uses the theory of random chance probabilities to choose representative sample locations. Random sampling is generally employed when little information exists concerning the material, location, etc. It is most effective when the population of available sampling locations is large enough to lend statistical validity to the random selection process. Since one of the main difficulties with random sampling deals with achieving a truly random sample, it is advisable to use a table of random numbers to eliminate or reduce bias (Appendix E).

Systematic Sampling

Systematic sampling involves the collection of samples at predetermined, regular intervals. It is the most often employed sampling scheme; however, care must be exercised to avoid bias, if, for example, there are periodic variations in the material to be sampled such that the systematic plan becomes partially phased with these variations.

A systematic sampling plan is often the end result for approaches that are initiated as random due to the tendency of investigators to subdivide a large sample area into increments prior to randomizing.

Stratified Sampling

Data and background information made available from the preliminary site survey, prior investigations conducted on site and/or experience with similar situations can be useful in reducing the number of samples needed to attain a specified precision. Stratified sampling essentially involves the division of the sample population into groups based on knowledge of sample characteristics at these divisions. The purpose of the approach is to increase the precision of the estimates made by sampling. This objective should be met if the divisions are "selected in such a manner that the units within each division are more homogeneous than the total population." The procedure used basically involves handling each division in a simple random approach.

Judgment Sampling

A certain amount of judgment often enters into any sampling approach used; however, this practice should be avoided whenever possible, especially if the data generated are likely to be used for enforcement purposes. Judgment approaches tend to allow investigator bias to influence decisions, and, if care is not exercised, can lead to poor quality data and improper conclusions. If judgment sampling does become necessary, it is advisable that multiple samples be collected in order to add some measure of precision.

Hybrid Sampling Schemes

In reality, most sampling schemes consist of a combination or hybrid of the types previously described. For example, when selecting an appropriate plan for sampling drums at a hazardous waste site, the drums might be initially staged based on preliminary information concerning contents, program objectives, etc. (judgment, stratified sampling), and then sampled randomly within the specified population groups (random sampling). Hybrid schemes are usually the method of choice as they can allow for greater diversity without compromising the objectives of the program.

Multiple Samples

Multiple samples need to be collected at any time legal action is anticipated. It is recommended that multiple samples be collected whenever possible. These additional samples are essential to any quality control aspects of the project and may also assist in reducing costs associated with resampling brought about by container breakage, errors in the analytical procedure, and data confirmation. The following is a list of the types of multiple samples required.

Sample Blanks

Sample blanks are samples of deionized/distilled water, rinsed collection devices or containers, sampling media (e.g., sorbent), etc. that are handled in the same manner as the sample and subsequently analyzed to identify possible sources of contamination during collection, preservation, handling, or transport.

Duplicates

Duplicates are essentially identical samples collected at the same time, in the same way, and contained, preserved, and transported in the same manner. These samples are often used to verify the reproducibility of the data.

Split Samples

Split samples are duplicate samples given to the owner, operator, or person in charge for separate analysis.

Spiked Samples

Spiked samples are duplicate samples that have a known amount of a substance of interest added to them. These samples are used to corroborate the accuracy of the analytical technique and could be used as an indicator of sample quality change during shipment to the laboratory.

Document Control/Chain-of-Custody

Strict adherence to document and data control procedures is essential from the standpoint of good quality assurance/quality control and should be instituted as routine in any hazardous waste investigation. It becomes especially important when collected data is used to support enforcement litigations. All collected information, data, samples, and documents must therefore be accounted for and retrievable at any time during an investigation.

The purpose of document control is to ensure that all project documents be accounted for when the project is complete. Types of documents considered essential include maps, drawings, photographs, project work plans, quality assurance plans, serialized logbooks, data sheets, coding forms, confidential information, reports, etc.

Chain-of-custody procedures are necessary to document the sample identity, handling and shipping procedures, and in general to identify and assure the traceability of generated samples. Custody procedures trace the sample from collection, through any custody transfers, and finally to the analytical facility at which point internal laboratory procedures take over. Chain-of-custody is also necessary to document measures taken to prevent and/or detect tampering with samples, sampling equipment or the media to be sampled. A detailed description of Document Control/Chain-of-Custody Procedures can be found in Appendix D.

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The complete report, entitled "Characterization of Hazardous Waste Sites—A Methods Manual: Volume II. Available Sampling Methods," (Order No. PB 84-126 929; Cost: $20.50, subject to change) will be available only from:
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