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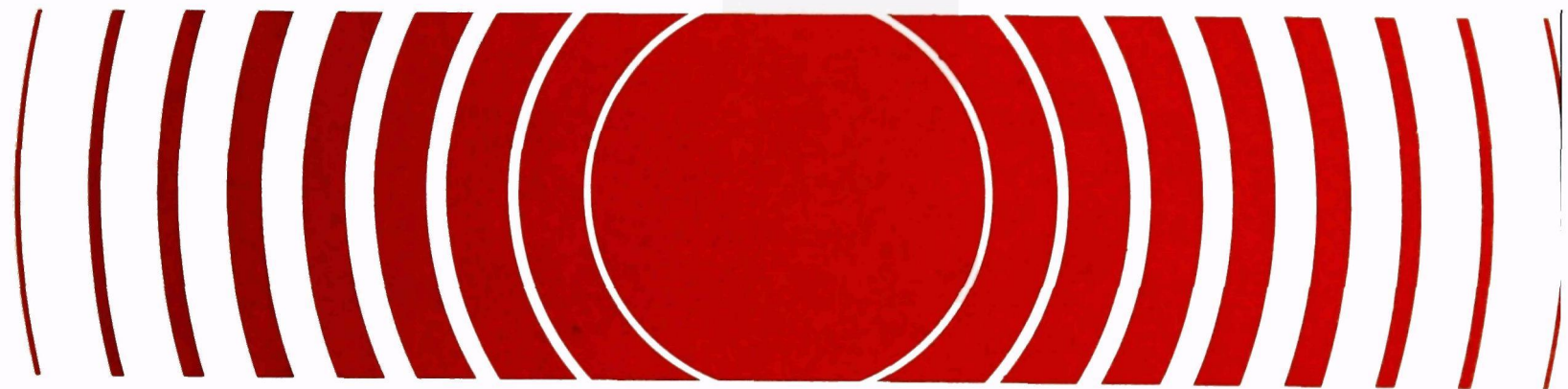
Sediment Monitoring at Deep-Ocean Low-Level Radioactive Waste Disposal Sites

Methods Manual

A METHODS MANUAL

for

SEDIMENT MONITORING AT DEEP-OCEAN

LOW-LEVEL RADIOACTIVE WASTE DISPOSAL SITES

edited by

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FOREWORD

In response to Public Law 92-532, the Marine Protection, Research and Sanctuaries Act of 1972 as amended, the Environmental Protection Agency (EPA) promulgated regulations in 1977 to control disposals of waste materials in the oceans. The EPA is currently developing revisions to the existing Ocean Disposal Regulations. The EPA Office of Radiation Programs (ORP) is developing site designation, waste package performance, and monitoring criteria applicable to ocean disposal of low-level radioactive wastes (LLW). The ORP is also preparing technical information reports to support LLW disposal criteria.

This report is a methods manual for monitoring sediments in the deep ocean. It is intended to be a frame of reference for baseline monitoring to characterize LLW disposal sites, and for site designation and trend assessment monitoring of sediments.

The Agency invites all readers of this report to send any comments or suggestions to Mr. David E. Janes, Director, Analysis and Support Division, Office of Radiation Programs (ANR-461), Environmental Protection Agency, Washington, DC 20460.

Richard J. Guimond, Director
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PREFACE

This manual contains methodologies for monitoring specific environmental parameters at LLW disposal sites. It includes procedures for 15 types of analyses and specific recommendations for shipboard operations related to the collection, handling, and storage of sediment samples. These analyses and recommendations are not necessarily permanent parts of the EPA regulations or criteria for the disposal of LLW on the seafloor, nor is the material included herein to be considered exclusionary: the manual is a working document that represents a step toward the eventual assurance that prudent site investigations will be conducted. Moreover, the methods presented are not to be considered definitive: analytical methods are constantly improving, new methods can be developed, and technology is advancing. The methods given do, however, provide a frame of reference and a starting point.

In some cases, more than one method is given for a particular analysis. This does not imply that the manual is intended to be a methods encyclopedia. Rather, it simply underscores the fact that alternative methods exist or, that for some analyses, more than one method is in common use.

This manual is a product of the efforts of many individuals. Contributors are: P. Colombo, M. Fuhrmann, and R. Pietrzak of Brookhaven National Laboratories and Associated Universities, Inc. in Upton, NY; R. Willingham and J. Nowland of the U.S. Army Corps of Engineers in Marietta, GA; K. Fanning of the University of South Florida in St. Petersburg, FL; and J. Booth, M. Bothner, J. Hathaway, F. Manheim, C. Parmenter, L. Poppe, and W. Winters of the Atlantic Marine Geology Branch, U.S. Geological Survey (USGS) at Woods Hole, MA. The compilation and editing of incorporated materials were accomplished by the USGS. The draft final report was transferred from the USGS NBI word processing system for editing on the EPA Office of Radiation Programs (ORP) word processing system by P. Cuny and W. R. Curtis of ORP. The report was then revised, as necessary, by Mr. Curtis and prepared for publication.

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CHAPTER 1

SELECTION OF SEDIMENT MONITORING CRITERIA

Introduction

The scientific suitability of a deep-ocean site for low-level radioactive waste (LLW) disposal depends on the type of radioactive waste material; the packaging parameters; the natural physicochemical characteristics of the site, including oceanographic factors (i.e., collectively, the local marine environment); and the waste's predicted impact on the biosphere, including food chain relationships.

The monitoring criteria presented in this document are those related to the physicochemical environment. The measurements included will provide guidance within this category for the site selection. These criteria, which include recommended measurements, were established because they provide information on the radionuclide retention capability of deep-sea sediment, which is the ultimate host medium for the LLW. The measurements also provide pertinent information on the geologic stability of the site, the penetrability and subsequent settlement of the waste packages, and on the corrosiveness of the environment with respect to the packaging material. Finally, the measurements will help to characterize the site for many other considerations which can be applied to modeling or other pertinent evaluation activity.

The measurements included in this manual provide a framework of scientific guidelines within which to evaluate a candidate LLW site's ability to retain radionuclides of concern over a specified time period and in a semiquantitatively acceptable manner.

Radionuclides of Concern

LLW typically contains a variety of radionuclides, many of which are present in small quantities and/or have very short half-lives. These nuclides are generally not considered to pose a serious health hazard per se. However, other nuclides may be considered "radionuclides of concern." Such nuclides are defined in terms of the following criteria: (1) half-life more than 5 years, (2) presence in relatively significant quantities, and (3) biological toxicity (Wild et al 1981). Radionuclides that are commonly present in LLW and that meet at least one of the aforementioned criteria are listed in Table 1. Most of these radionuclides will be eliminated or are present in negligible amounts. However, three of the nuclides that will be present in the waste package and meet all the criteria are cesium, cobalt, and strontium (specifically the ^{137}Cs, ^{60}Co, and ^{90}Sr isotopes).

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Table 1. Radionuclides Commonly Present in LLW

Name	Isotopic Symbol	Half-life (Years)
Cobalt	^{60}Co	5.3
Tritium	^{3}H	12.3
Plutonium	^{241}Pu	14.4
Curium	^{244}Cm	17.6
Strontium	^{90}Sr	28
Cesium	^{137}Cs	30.2
Curium	^{243}Cm	32
Plutonium	^{238}Pu	87
Nickel	^{63}Ni	92
Americium	^{241}Am	445
Carbon	^{14}C	5,730
Plutonium	^{240}Pu	6,580
Americium	^{243}Am	7,650
Niobium	^{94}Nb	20,000
Plutonium	^{239}Pu	24,110
Nickel	^{59}Ni	82,000
Technetium	^{99}Tc	210,000
Cesium	^{135}Cs	2,000,000
Neptunium	^{237}Np	2,100,000
Iodine	^{129}I	16,000,000
Uranium	^{235}U	710,000,000
Uranium	^{238}U	4,510,000,000

Factors That Control Radionuclide Retention

The primary barrier to radionuclide migration is the waste package (the matrix and container) itself, but because the package lies on or in the sea floor, an additional barrier is available: the contiguous sediment. The relative effectiveness of this natural barrier depends on the portion of the package that is in contact with or embedded in the medium and the retention potential of the sediment itself. The area of contact or embedment may be roughly estimated a priori by using certain geotechnical parameters and geologic information. The area of conflict is also the implicit justification for the recommended measurements, which serve as a means to estimate the effectiveness of those sediments as a barrier.

Numerous factors control the inherent ability of the sediment to retain radionuclides. Onishi et al (1981) have examined selected radioisotopes and the factors that control their uptake in natural environments. They show that the ability of marine sediments to sorb these isotopes is governed by the type and quantity of sorptive minerals, complexing ligands, amorphous oxides, organic matter, and competing ions; pH; Eh; and the potential for colloid formation.

Recommended Measurements

The measurements and associated methods in this manual are intended to provide either direct or indirect information with which to judge the radionuclide retention potential of a candidate LLW site. In recognition of the multidisciplinary nature of these assessments, the manual is divided into three parts: Geological, Geochemical, and Geotechnical. Guidelines for proper sample collection and treatment aboard ship are also included.

The methods presented herein are either generally accepted as standard and widely used by laboratories concerned with batch analysis, or they represent state-of-the-science analytical procedures for those measurements for which there are no standards or common methods. Although alternative methods are available in many cases, use of these methods provides a basis for comparison and evaluation and promotes uniform data reporting.

The types of measurements include those currently listed in current ocean disposal regulations, those additonally reommended because of the specific monitoring needs pertaining to the disposal of packaged LLW at depths of 4,000 meters or more (this depth is recommended by the International Atomic Energy Agency pursuant to the London Dumping Convention agreement, of which the United States is a signatory), and those that are

presented as optional. A document entitled "Sediment Monitoring Parameters and Rationale for Characterizing Deep Ocean Low-Level Radioactive Waste Disposal Sites" (EPA 520/1-87-011) provides more background information and detail on these measurements. The following sections present each type of measurement and a summary of that measurement's bearing on radionuclide retention in marine sediments.

Geological Measurements

(1) Sediment Texture is a key variable for site evaluation and is a required measurement under existing ocean disposal regulations. Grain-size data may be used to estimate basic radionuclide retention (i.e., sorptive characteristics), to correlate data from other fundamental geotechnical measurements (which in turn can be used to estimate package embedment), and to obtain an indication of geologic stability (i.e., recent or active dynamic processes on the seabed). Grain-size data often correlate with organic content and other geochemical variables, may also be used to calculate mineral percentages, and generally are the most versatile of all the indirect monitoring methods.

(2) Mineralogy is important because of the sorption properties of several of the radionuclides of concern, including cesium and strontium. Sorption is primarily dependent on cation exchange and large surface areas. Sediments rich in zeolites, smectites, and other clay minerals have a high sorption potential for the retention of the radionuclides relative to sediments dominated by less sorptive minerals such as quartz, feldspars, calcite, and nonclay phyllosilicates (i.e., muscovite or biotite). Moreover, identification of minerals that may have economic potential could disqualify a site for LLW disposal. An accurate inventory of the mineralogical suite is therefore required under the current ocean disposal regulations.

(3) Radiography of sediments provides information that pertains to radionuclide retention, geologic stability, and package embedment. Bioturbation, for example, which is detectable in x-radiographs, can be evaluated as an indicator of vertical mixing of the sediment (and vertical transport of radionuclides). The presence of laminae, clasts or sand, and graded beds can also be detected, all of which bear on the geologic stability of the site.

Geochemical Measurements

(1) The distribution coefficient (R_d) reflects the ability of a sediment to sorb a selected radionuclide under specific (e.g., in-situ) conditions. It is therefore a direct measure of the retention potential in a proposed site. It is defined (Pietrzak et al 1981) as the ratio of specific

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activity in the sediment phase to that in the liquid phase for the radionuclide of interest. That is,

$$R_d = \frac{\text{sediment activity/weight of sediment}}{\text{liquid activity/volume of liquid}}$$

Thus, the greater the R_d value, the greater the nuclide retention by the host sediment. The method of R_d measurement in this manual provides the only direct measurement of radionuclide retention potential in a candidate seafloor site. However, because the quantitative effectiveness of scavenging (sorbing nuclides from solution) depends on many factors such as mineralogy, redox state, and the presence of competing ions, it is essential that a profile is developed that includes the "fluff" (the topmost surficial sediment and nepheloid layer particulates) as well as sediment that may be at the limit of waste package penetration.

Retention may also be examined in terms of diffusion. The rate of radionuclide diffusion, from a source below the sediment-water interface into the water column, may be an important parameter to measure for many nuclides with low R_d's or for those that are particularly abundant. Accordingly, the measurement of diffusion coefficients is under consideration for possible inclusion in this and related documents.

(2) Oxidation-Reduction Potential

Three separate methods are given in this manual for evaluating the redox state of the sediment: (1) direct measurement of Eh, (2) measurement of sediment Fe and Mn concentrations in profile, and (3) measurement of nitrate porewater concentration in profile, which is the most accurate, complicated and expensive of the three. Retention of several radionuclides of concern, including ^{60}Co, ^{99}Tc and ^{237}Np, is significantly affected by redox state, making this parameter one of the key elements in a LLW site investigation. Redox state changes from oxygenating (+) conditions at the sediment surface to reducing (-) conditions at subbottom depths from several centimeters to several meters in deep-ocean sediments (Schmidt 1979, Carpenter et al 1983, and Wilson et al 1983)). Thus, a profile must be developed to determine the position of the redox-state boundary in the sediment column and the relative position of this boundary to waste package penetration depth.

In-situ redox potential of deep-ocean sediments is extremely difficult to determine. Redox state is sensitive and highly variable, and the removal of samples from their natural geochemical environment may compromise the validity of subsequent shipboard or laboratory measurements ashore, particularly if the sample has been exposed to an oxygen-rich environment.

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A sulfide sulfur test to assess redox state may be included in a subsequent version of this manual. Because the reduction of sulfate to sulfide signals the presence of anaerobic conditions, this test, which is simple and relatively inexpensive, could provide, as do the other three redox methods, information on the position of the boundary between oxygenating and reducing conditions. Moreover, because sulfide formation requires the presence of both iron and sulfate-reducing bacteria, which is the case when a steel waste drum is in a reducing environment, corrosion of the drum occurs through cathodic depolarization (Uhlig 1971). This affects the efficiency of the primary retention medium, the waste package. The sulfide sulfur test may therefore provide predictive information on waste package performance as well as redox state. Despite this additional utility, however, the sulfide sulfur test is considered inferior to the other three redox tests because it requires interpretation of the sediment history, and consequently is generally a less reliable test and specifically a less accurate test with regard to the placement of the oxygenation-reduction boundary. Accordingly, the sulfide sulfur test should only serve as a backup to one of the other types of measurement.

(3) Hydrogen ion activity (pH) affects retention of strontium, cobalt, plutonium and other important radionuclides because it affects their solubility (Onishi et al 1981). pH is a standard geochemical descriptor and is necessary for understanding or predicting reactions. To date, most measurements indicate that pH may not vary significantly in deep-sea sediments, but recent in-situ data suggest that it may be more variable than earlier studies indicated.

As presented in this manual, pH is a simple measurement utilizing a standard pH meter and probe. The measurement may be done in conjunction with Eh measurements. As with Eh, however, measurement results may not be representative of in-situ conditions unless great care is taken. In the case of pH, outgassing must be avoided, because the buffering capability of the porewater at the probe site may be affected.

(4) Total organic carbon

The radionuclide retention capability of a sediment can be adversely affected by organic matter. For example, it has been demonstrated at LLW land sites that ^{60}Co can form complexes with organic constituents and that these complexes are not easily sorbed (retained) by the host medium. In effect, the geologic barrier is rendered inefficient by such complexes. The isotopes ^{90}Sr, ^{239}Pu and others also form complexes with organic constituents (Onishi et al 1981); although a general lack of data on these nuclides precludes predictions about retention, they too may affect the retention capability of the host sediment. Measurement of organic carbon is required under the current ocean dumping regulations.

Geotechnical Measurements

(1) Index properties

Natural water content, liquid and plastic limits, and grain specific gravity constitute the geotechnical index property suite for this methods manual. These mass physical properties are a basis for sediment classification; they correlate with textural and compositional sediment attributes and give insight into the stress history, stress behavior (comprassion index), permeability and numerous other engineering characteristics of sediments. More specifically, index property data may be used to provide a first-order prediction of waste package penetration and settlement into sediments. They will also provida data on the geologic stability of a LLW site and a first-order approximation of its retention potential.

(2) The vane shear test measures undrained shear strength of a cohesive (fine-grained) sediment. Both "natural" and remolded strengths are normally determined on a sample. The former gives an indication of the maximum strength and the latter of the minimum strength of the sediment. This test has direct utility in evaluating waste package embedment, and also may be used to assess geologic stability and the degree of compaction of the sediment. The test is currently optional, but is being considered as a recommended measurement for LLW site monitoring if package burial becomes a disposal option.

(3) One-dimensional consolidation tests indicate stress-strain relationships in a sediment and thus are directly applicable to settlement analysis of an applied load such as a waste canister. In addition, the test provides information on the maximum past stress (overburden) on a site, which has implications regarding erosion, mass movement, sedimentation rate, excess pore pressure, and other factors that bear on geologic stability. Consolidation testing is optional. The method presented in this manual (constant-rate-of-strain) is the most rapid of the common methods, and is relatively inexpensive.

(4) Static triaxial compression tests can determine drained and undrained strength parameters as well as stress-strain relationships. It is appropriate for analyzing canister penetration and for estimating subsequent settlement under the load conditions imposed by the waste package. Results of this test also may be used in a variety of slope stability analyses and other evaluations that bear on geologic stability.

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CHAPTER 2

SAMPLING AND SHIPBOARD RECOMMENDATIONS

Introduction

The only general requirement for sampling is that the upper 30 cm of sediment must be recovered. However, if the recovered sample is to be truly representative of in-situ conditions, it must be collected with tools of optimum design and receive appropriate treatment during the pre-analyses phase. These requisites are often compromised by cost and time constraints, and by shipboard and laboratory pragmatisms. Thus, a necessary preliminary to LLW disposal site investigations is to define a level of sample quality that is both acceptable and attainable within the practical constraints of field and laboratory operations. This chapter provides guidelines and rationales for sampling and sample treatment that support the analytical methods found within this manual.

Sampling

Some disturbance or alteration of a sediment sample during conventional sampling activities is inevitable. The simple act of removing a parcel of sediment from its natural environment and transporting it to the surface precludes the possibility of ever obtaining a completely undisturbed sample because in-situ stresses are released during recovery. The effect of this on sample quality is especially obvious for a sediment that is overprocessed in-situ or one that contains dissolved gases which may ebullate as hydrostatic pressure is reduced from more than 400 atmospheres (at approximately 4,000-meters water depth) to 1 atm on deck. However, if such alterations are limited to changes in stress, the sampling activity was successful.

Although the dramatic change in stress cannot be obviated, unless a pressurized sampling system is developed, it may only be detrimental to overall sample quality in rare circumstances. In most cases, other sources of disturbance have the most affect on sample quality. These sources include varying degrees of shock, sediment compression, skin friction and other actions that accompany sampler penetration; as well as the tension-release and "flow-in" changes in stress that may accompany sampler withdrawal. These gross physical disturbances disrupt sediment layering, which affects radiograph interpretation, alters strength and consolidation properties and, potentially, affects analyses that focus on the sediment profile (i.e., texture, mineralogy and the suite of geochemical measurements. The

fundamental goal of sampling -- to preserve in-situ integrity of sediment mass to the highest degree possible -- can be largely realized, however, by judiciously selecting the proper type of sampling system.

A number of instruments have been developed for collecting a sediment sample from the deep sea with a minimum of disturbance. Practical considerations, however, limit selection to box corers and large-diameter "gravity" corers, because other systems are either too expensive (e.g., pressurized corers, and bottom-sitting platform corers with fixed pistons), may cause too much disturbance (e.g. grab samplers and piston corers), or have some other problem. Box corers and gravity corers meet the penetration and distrubance criteria, do not require an inordinate amount of deckspace or special ship rigging, are readily available and are relatively straightforward to operate and maintain. Box corers that are particularly suited include the Soutar Box Corer (Soutar et al, 1981), which features a slowed entry, and the Hessler-Sandia MK-3. Though relatively expensive and cumbersome compared to gravity corers, box corers offer the advantages of large sample volume and reliability, and are unsurpassed with regard to the quality of sample they recover. Moreover, they lend themselves to subcoring, which is a noteworthy advantage in a multidisciplinary activity such as LLW disposal site monitoring.

Gravity coring is quick, simple, and inexpensive. It also offers the advantage of speed: the elapsed time between the corer breaking the sea surface upon recovery and storage or the start of processing of the core sample can be less than 5 minutes, which may be an important factor for some types of geochemical analyses. Some gravity corers even offer special features, such as hydraulic damping during entry (Pamatmat 1971), which further enhances the chances for high sample quality. To generally achieve optimum sample quality, one should select a corer model with an inside diameter of at least 5 cm. It should not require a cutter (nose-cone), internal core catcher or liner. A Benthos model 2171, hydroplastic corer (Richards and Keller 1961) with external core catcher, or equivalent, is recommended. If a gravity corer is used, it may be necessary to collect replicate cores at stations. The actual time required for this extra coring should not be considered a prohibitive disadvantage per se. Further, such activity provides an opportunity to examine local variability of the sediment because the replicates would be recovered from different, though proximal, locations.

Regardless of the coring system used, certain operational caveats apply: (1) entry and withdrawal of the corer from the sea bed must be done as slowly as possible to enhance recovery of a high quality sample; (2) a pinger, attached to the corer, is essential for estimating distance to the sea bed; (3) a reliable means for stabilizing the corer when it breaks the sea surface should be readily available to ensure that the sample is not jerked around or banged into the ship or any of the deck gear; (4) coring should not be attempted when the sea state is high enough to cause difficulty in handling coring equipment or cores during collection or recovery operations, to prematurely trigger a core descending to the seafloor, to allow double entry (repeat penetration) into the sea bed, or to anyway compromise core quality; and, (5) the coring tube and liner/s/ should always be kept clean and free from potential contaminants that could affect the collected sample/s/. Corrosion products, such as rust, can not only affect the results of geochemical analyses (e.g., Fe), but they can also alter texture and mineralogy measurements.

A more complete discussion of coring and related factors, as well as an extensive bibliography on the subject, are provided by Lee (1985). Other pertinent references include Lee and Clausner (1979), Rosfelder and Marshall (1967), and Hvorslev (1949).

Handling

Once the coring device is brought to the sea surface, extreme care must be exercised. The core should be maneuvered slowly to the deck or its cradle to avoid accidental bumping, which causes physical disturbance, and should be set down as gently as possible. Enough hands should be available to guide the suspended corer and ensure that it does not get out of control. Core length and penetration distance should be measured and recorded as soon as the core is safely on board. The core should be prepared quickly for storage (wrapped) or shipboard laboratory work (moved to a "constant environment" location) to avoid adverse effects (changes due to temperature, evaporation, drainage, vibrations and other factors) from potential accidents due to shipboard activities or the weather. Cores should always be stored in an upright position if contained in liners. If the core is too long to store vertically, it should be sectioned for storage with each section capped and sealed.

If a box corer was used, the cored sediment must be processed immediately. Otherwise it may begin to drain. The sediment sample should be subcored by smoothly inserting large-diameter (|6-7 cm I.D.), thin-walled (1-3 mm) tubes that have been sharpened on the "cutting" end. It is recommended that the tubes be made of plastic (e.g., polycarbonate) or some other inert material to avoid chemical reactions that may alter geochemical, or other, properties. Common core liner is usually used. After the subcore tubes have been inserted, the outside (box) corer may be taken apart and the rest of the original core material removed. Once free, the subcore tubes should be cleaned and inspected. They should always be kept vertical. If a particular core is to be used for detailed geochemical profiling, it may be desirable to maintain several centimeters of seawater over the sediment to mitigate disturbance of the sediment-water interface during handling. Alternatively, the supernatant seawater can be siphoned off and stored for future analysis. For other types of analyses, any space between the sediment surface and the top of the liner should be plugged to prevent future movement of the core in the liner or disruption of the sediment surface. The plugs should be made of light-weight nonabsorbing material, such as close-celled styrofoam or wax. Next, the tube should be capped (commercial plastic or rubber end caps are suggested) and the caps should be taped in place with several wraps of plastic electrical tape. Care must always be taken not to invert the subcore during handling, which can cause severe disturbance if the sample is not "tight" in the tube or if the sediment is "soupy." The subcore must not be tamped on the deck because tamping artificially compacts the sediment and changes its strength, consolidation, and water-content-related properties. In addition, its gross structure and sensitive geochemical profiles may also be adversely affected. All core tubes, caps, and utensils should be cleaned carefully with appropriate acids and/or solvents before use. This cleaning is not standardized; the reagents vary and depend on the composition of the plastics.

Because the subcores are comparatively short, there is less hydrostatic head and thus they are less apt to leak than longer cores. However, surface samples are typically high in water content and core ends should be waxed as further protection against leakage. If the cores are not scheduled for immediate analysis, the entire tube should be waxed to retard evaporation through the tube walls, which, if plastic, tend to be pervious. The tubes should be handled and stored in the in situ position and labeled indelibly with identification information and an "up" arrow.

The subcoring technique works well for box cores, but is unnecessary with gravity cores. All statements made previously on the handling of subcores apply to gravity cores if they are the type that employ plastic pipe as a barrel (note that the two recommended gravity coring systems are such types).

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If it is desirable to collect long cores (i.e., longer than 11.5 meters), or for other reasons use of a core liner is appropriate, care must be taken when the filled liners are extruded from the core barrels. They should never be hammered or jerked unless such action is absolutely necessary to free the liner. If the core is to be sectioned, first cut the liner. This should be accomplished without unnecessary vibration or pressure on the liner because such disturbance is transmitted to the core. This can be done by using tools especially manufactured for cutting plastic pipe. It is suggested that such cuts be made between clamps. Clamps hold the liner securely and prevent it from flexing as pressure is applied. Without clamps, the portions of the core near the cut will be disturbed unless a very rigid liner is used. A hacksaw may also be used to cut the liner, but it is not preferred because of the vibration caused by its use and because it may affect texture analysis locally if plastic shards get into the sediment. After the liner has been cut, the sediment should be parted with a wire saw. The sections should be no more than 1.5 m (approximately 5 ft) long, and should be cut much shorter (approximately 0.5 m) if long-term storage (more than a month) is anticipated. The sections should be capped, waxed, and labeled as described above.

Whether the original cores were lined or unlined, all core samples should be adequately protected from additional disturbance or alteration at this stage. They may also be x-radiographed on the ship to check for disturbance. This is desirable because if problems are discovered, recoring is possible. However, it is generally impractical.

Shipboard analytical work should always be seriously considered during cruise planning. Samples intended for triaxial, consolidation, or other complicated testing may need to be prepared for safe transport because it is difficult to perform these tests at sea, but there are numerous tests, such as nitrate analysis, Eh/pH measurements, vane shear tests, and other activities (i.e., subsampling) that should be done at sea to avoid disturbances or alterations related to further handling and storage of the samples. In addition, shipboard testing provides site information while still in the field, and smaller subsamples are more easily protected against evaporation or other changes than whole cores or core sections.

Storage

Proper storage of the sealed sample tubes, whether at sea or ashore, is an essential part of the pre-analysis activity. Of paramount importance in this regard is storing the samples at the proper temperature: all samples must be refrigerated. It may even be desirable to freeze samples dedicated to certain geochemical tests, particularly if shipping is required. Refrigeration

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temperature should be between 1-5 °C for general preservation, and, because in situ temperatures at depths greater than 4000 m are approximately 1 °C, storage at this temperature would match in situ conditions. However, freezing of geotechnical samples must be prevented, so care must be taken to avoid accidental freezing if 1 °C is chosen as the storage temperature. Storage in an air-conditioned environment is acceptable for a short period of time, such as while at sea, if refrigeration is not available, but is not recommended. Temperatures even at this level (15-22 °C) cause expansion and "softening" of the sediment (Mitchell 1976), accelerate bacterial and other organic productivity, and promote evaporation; all of which are detrimental to sample quality. The storage area should ideally be kept at 100 percent relative humidity as an additional safeguard against evaporation. In fact, from core retrieval to storage, all practical safeguards must be taken against evaporation because this process can drastically alter many geochemical and geotechnical properties, and even change the texture and mineralogy of authigenic minerals (such as gypsum) which could begin to form. Sun, or other light, that fosters organic growth should not access the area unless the tubes or liners are opaque. For short periods of time (a few weeks at most) strict humidity control may not be as critical.

The core tubes should be stored vertically upright with the sediment surface at the top; the tubes should be well-padded underneath, and tightly secured. The padding and secure fastening are particularly important at sea because the samples need to be isolated from high-frequency (motor-induced) and low-frequency (motion-induced) vibrations which can cause dynamic loading and settlement in the tubes. The core tubes should not be stacked. Samples that are a product of shipboard subsampling and intended for geotechnical index property testing, if properly sealed in plastic bags and/or cans containing a wet tissue, need not be protected so rigorously, but refrigeration is highly recommended.

Shipping

All samples should be sent to the laboratory as soon as they reach port. Optimally, they should be hand-carried to their destination in padded cases. If there are too many samples to carry and long-distance shipping is unavoidable, air freight is preferred to trucking. Air freight is faster and subjects the samples to less vibration; storage temperature may be stipulated within reason, but for short periods of time this is generally not necessary. No matter what the conveyance, the tubes and other samples should be shipped in their proper orientation and in sturdy, well-padded boxes. The boxes should be marked "fragile" and have "up" arrows clearly in view. Commercially available tip indicators should be affixed to both the inside and outside of each box so that if the tubes are inverted or on their side during transport, it will be known. If possible, the boxes should be constructed such that the preferred orientation is obvious.

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After they arrive at the laboratory, the samples should be stored as discussed and the analyses should begin as soon as possible. Storing cores for more than a few months should be avoided because aging, which alters the properties, can occur relatively quickly (Mitchell 1986).

Summary

The properties of marine sediments are extremely vulnerable to alteration during sampling and subsequent activity. Seemingly minor improprieties during field work may render part of a derived data set worthless or, perhaps worse, leave the data quality uncertain. Accordingly, all reasonable precautions should be taken to avoid physical, chemical, or biological changes in the samples, and every effort should be made to complete the analyses of the samples as soon as possible.

In general, the following guidelines should be adhered to: (1) samples should not be jarred, tamped, vibrated, or pressure-loaded in any way; (2) storage temperatures should be kept near freezing, or frozen in some cases; (3) humidity should be as high as possible, and any circumstance that favors evaporation or drainage should be avoided; (4) the storage area should be free of light wavelengths that favor organic productivity unless sample tubes are opaque; and, (5) cores should be transported and stored as close to their in situ orientations as possible. If these guidelines are followed, and if proper sampling equipment has been used, the investigator may be reasonably sure that the data are as representative of field conditions as possible.

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GEOLOGICAL METHODS

CHAPTER 3

TEXTURE

Introduction

There are four main reasons for performing particle-size analyses on sediments (Blatt et al. 1972): (1) the grain size is a basic descriptive measure of the sediment; (2) grain size distributions are characteristic of sediments deposited in certain environments; (3) detailed study of the observed grain-size distributions often yield information about the physical mechanisms occuring during deposition or diagenesis; and, (4) grain size can often be related to other properties (i.e., permeability or stability), and variations in these properties may be predicted from variations in grain size. With this in mind, the fundamental objectives of a grain-size analysis are to accurately measure individual particle sizes, or hydraulic equivalents, to determine their frequency distribution, and to calculate a statistical description which adequately characterizes the sample.

The accuracy of these measurements is limited by the capability of the operator, the sampling (see Chapter 2) and measuring techniques, and the equipment. Care and attention to detail must be exercised to achieve the best possible results. As with most types of analyses, there is no ultimate technique or procedure that will produce the most desirable grain size data for all cases. Several types of analyses have been developed over the years to accommodate the types and sizes of samples and the reasons for doing the analyses.

The recent development and commercial availability of inexpensive microcomputers allows sedimentologists to construct complete computerized particle-size analysis systems (Poppe and others 1985). The major advantages of using these systems are the time-, labor-, and cost-saving functions they afford. Most of the laboratory equipment and procedures, and all of the data processing described herein, may be adapted to these computerized systems.

Procedure

1. Because the same analysis is not done for each requestor and because the size data often become part of a data base, there must be some formal system for recording what analyses have been completed on each sample and for whom they were performed. To this end, the use of "REQUEST FOR ANALYSIS" and "SAMPLE ID" forms (Figs. 1 and 2) are recommended as organizational aids. These completed forms should be included when

SEDIMENTATION LAB

REQUEST FOR ANALYSIS

SUBMITTER:_____

Cruise ID _____ Project ID _____

NO. OF SAMPLES:_____

DATE SUBMITTED:_____

DATE RESULTS NEEDED BY:_____

WORK REQUESTED:_____

_____

_____

_____

SPECIAL INSTRUCTIONS:_____

_____

_____

_____

AFTER JOB IS COMPLETED:

DISCARD BULK:_____

RETURN TO SUBMITTER:_____

PURPOSE OF INVESTIGATION:_____

_____

_____

_____

_____

_____

PAGE ___ OF ___ PAGES

Figure 1. Example of a REQUEST FOR ANALYSIS form.

FIELD NO.	LAB NO.	LOCATION DEGREES AND DECIMAL MINUTES (N-S OR E-W)		WATER DEPTH (M)	SAMPLING DEVICE	AREA	TOP DEPTH (CM)	BOTTOM DEPTH (CM)
		LAT.	LONG.					

Figure 2. Example of a SAMPLE ID form.

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samples are submitted for analysis. Appropriate identifers include: requestor, cruise identification (ID), project ID, work requested, purpose of investigation, sample ID, latitude and longitude of collection site, water depth, top depth, bottom depth, sample device, and sampling area.

After the forms are completed, a unique lab number should be assigned to each sample. This number may consist of two letters followed by three numbers (e.g., AA795), or of sequential listing developed by the lab involved.

2. If the whole sample is not to be used, the sample is split by one of three methods: a micro-splitter, cone and quarter, or random bulk. The method selected for a given analysis will be determined by the size of the sample, its homogeneity, and the degree of accuracy that is required. As a general rule, the larger the analyzed sample, the more accurate the grain-size analysis. However, unless a sample contains abundant medium to coarse gravel, a 50g split is usually sufficient. Larger samples are more time consuming to analyze and do not provide significantly more reliable results.

3. Place the split sample in a preweighed 100ml beaker. These beakers should have previously been enscribed with a unique number, therefore requiring no additional labels (which would alter the total weight of the beaker). Dry the samples in a convection oven at 100 $^{\circ}$C. This temperature will drive off unbound water without affecting the grain size. When the samples are dry (overnight is usually sufficient), place them in a desiccator to cool and then weigh them. Gross sample weight minus the weight of the beaker gives the net sample weight.

4. Whole or fragmented calcite secreting micro- and macro-organisms can bias the grain size distribution if they occur in significantly high concentrations (greater than 5 percent). Their presence alters the textural data and complicates interpretation of sedimentary transport and deposition. Calcite or aragonite may be dissolved selectively using cold, dilute (10 percent) HCl or a 5 pH, NaOAc buffer (Jackson 1956). After the carbonate has been dissolved, the HCl or NaOAc buffer must be removed by multiple decantations or centrifugations using a buffer to remove the salts and distilled water to remove the buffer. Care must be taken to use these dissolution techniques only when detrital carbonate is absent. It is often easier to remove the fragments of biogenic carbonate manually from the coarse fraction (see below) than to treat the whole sample.

5. The removal of organic matter is necessary for complete dispersion of the clay and, in sediments with high organic content (greater than 5 percent), to prevent the organics from being counted as part of the sample, which would bias the

grain-size distribution. The sample is placed in a 600ml beaker and a small volume (approximately 10 ml) of 30 percent hydrogen peroxide is added. The sample is stirred and, if necessary, water is added to slow the reaction and prevent bubbling over. More hydrogen peroxide is added until the dark color of the organic matter has largely disappeared; then the sample is washed three times with a NaOAc buffer of pH 5 and once with methanol to remove the remaining released cations.

6. To prevent flocculation of the sediment and to give effective dispersion of the sediment during pipet analysis, the soluble salts and exchangeable polyvalent cations are removed by decantation or centrifugation with distilled water.

7. If the samples have been decalcified, treated with hydrogen peroxide, or desalinated, repeat Step 3 and recalculate the post-treatment net sample weight. Subtracting this value from the original will determine the weight of the removed constituent.

8. Wet sieve the sample through a 63 micron, American Society for Testing Materials (ASTM) #230 sieve to divide the sample into coarse (sand and gravel) and fine (clay and silt) fractions. A sodium hexametaphosphate solution (a 1,000ml beaker of Calgon containing 80ml of formaldehyde for each 5 gallons of distilled water) is recommended for wet sieving if an electronic particle counter (e.g., Coulter Counter) is to be used in the fine-fraction analysis. This solution acts as a dispersant and electrolyte, which is necessary when electronic particle coulters are used. A weaker electrolyte solution (0.5 percent) may be used if the fine fraction is to be analyzed by pipet. A rubber spatula and a squeeze bottle of the calgon solution provide the best sieving results. The coarser sand and gravel fractions are retained on the screen while the finer silt and clay fractions are collected in the catch pan. Place the coarse fraction in a preweighed 100ml beaker and the fine fraction in a Mason Jar. Wet sieve, using only enough calgon solution to fit in a single 32-oz Mason Jar to prevent any possible fractionational biasing of the fine fraction.

9. Dry the coarse fraction in a convection oven at 100 ^{o}C. When the samples are dry (overnight is usually sufficient), place them in a desiccator to cool before weighing them. Gross coarse weight minus the weight of the beaker gives net coarse weight.

10. Most of the biogenic calcite found in a sample is commonly in the form of coarse pelecypod or gastropod shell fragments. It is often easier and less time consuming to remove this carbonate manually from the sample and reweigh the now decalcified sample to determine the new net coarse weight. Remember, the weight of the carbonate must be subtracted from the net sample weight before entering the data into the computer.

11. The coarse fraction is usually determined by use of a settling tube (for a description of a typical settling tube, see Schlee 1966). However, if this fraction weighs less than 5 grams or if it contains greater than 5 percent foraminifera, which will not settle properly in a sedimentation column, sieves must be employed. If the coarse fraction grain-size distribution is to be determined by sieving, assemble a bank of sieves (see Table 2 below). A bank of sieves generally consists of a cover, the -1, 0, 1, 2, 3, and 4 phi sieves, and a catch pan. The bank of sieves is agitated in a shaker (such as a Ro-Tap) for at least 15 minutes. After sieving, weigh the sand and gravel fractions, record the weights from each phi class, and calculate the relative percents of the sand-fraction phi classes and the relative percents of the gravel-fraction phi classes. These data, per se, are normally entered directly into a computer or are manually combined with the fine-fraction data to obtain an overall complete grain-size distribution.

TABLE 2. Correlation of grain size phi classes with sieve sizes and numbers for A.S.T.M. and Tyler mesh sieves.

****

PHI CLASS	NOMINAL SIEVE OPENING (mm)	SIEVE SIZES ASTM #	SIEVE SIZES TYLER #	SIZE FRACTION
4	.062	230	250	
3	.125	120	115	
2	.250	60	60	SAND
1	.500	35	32	
0	1.000	18	16	
-1	2.000	10	9	
-2	4.000	5	5	
-3	8.000	0.3125	2.5	GRAVEL
-4	16.000	0.625	0.624	
¬5	32.000	1.25	-	

****

12. If the sand-fraction grain-size distribution is to be determined by a settling tube technique, the gravel-fraction distribution (if present) must still be determined by sieve analysis. Separate the dry sand and gravel fractions by using a 2.0mm (-1 phi) sieve, and weigh the gravel fraction. Net coarse weight minus the gravel weight gives the sand weight. Assemble a bank of gravel fraction sieves; then sieve to separate and weigh each phi class; record the weight; and, calculate the gravel-fraction relative percentiles.

13. The settling tube (e.g., Schlee 1966) provides a means for rapid size analysis of sand-sized material by settling the grains through a column of water (Fig. 3). One settling tube design is based on using the pressure differential between two columns of water that have a common head. The change caused by the introduction of sediment within one of the columns is measured by a transducer. Results are fed either to a strip chart recorder or to an analogue-to-digital converter, and relayed to a computer. As the sediment settles past the pressure transducer port, the pressure differential decreases with time. Because the sedimentation rate, in accordance with Stoke's Law, is a function of grain size, one can interpret the sand-fraction grain-size distribution from the variation in pressure differential. Because the design of this type of settling tube is common, a procedure and comments for use of such a device are given below.

A warm-up time of about 5 minutes is required for the transducer. During this time the operator should check the system pressure lines for air bubbles and note the settling column water level. Remove all air bubbles from the lines and raise the water level to 3-5 mm above the settling tube (see Fig. 3). The operator usually has the option of introducing the sample by using the automated flipper or by manually adding it with a tablespoon (this is generally true for most automated settling tubes). Both methods require practice to achieve reproducibility, but the results are equally accurate and comparable.

A micro-splitter is used to obtain a sample of 5-10 g. Optimal size is about 8 grams. Samples less than 5 g generate too weak a signal from the pressure transducer. A weak signal may be diluted by electrical and mechanical noise, causing greater error in the reproducibility of the data. Samples larger than 10 g are more apt to form density currents down the sides of the settling tube or, upon introduction, to form clumps of finer sediment which act as much larger particles.

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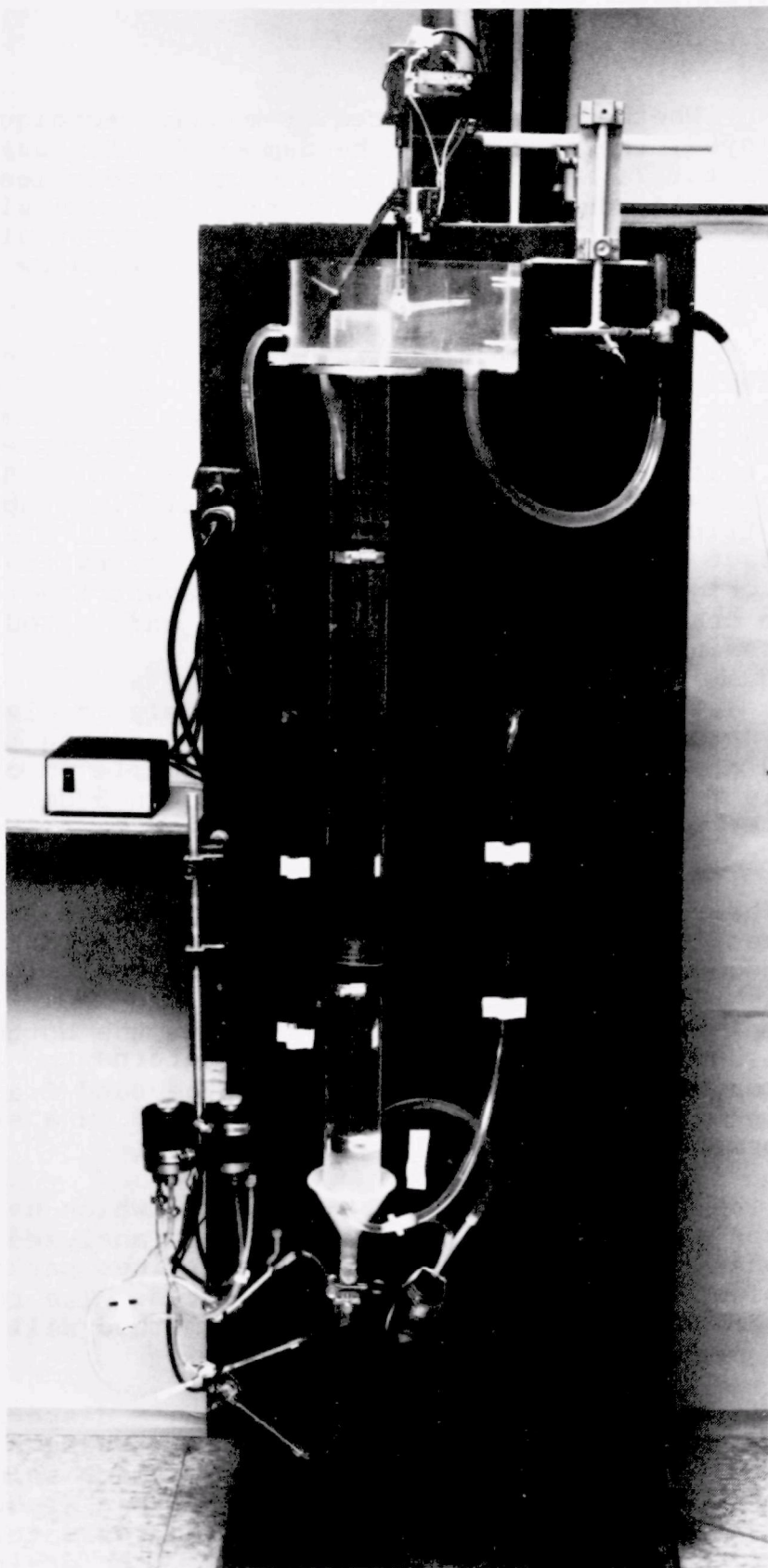
Figure 3. Differential pressure settling tube for sand-fraction analysis.

Whether the automated or manual technique is employed, the sample must be dampened with just enough water to: (a) afford enough intergrain cohesion to help the sample adhere to the flipper; (b) insure simultaneous introduction of the sample; and, (c) prevent air from becoming trapped in the sample, which may slow the settling rate of the particles.

If the automatic flipper technique is selected, place the sample on the flipper using a tablespoon, flatten the top of the sample to less than 1 cm in height, and dampen the sample with an eyedropper. When the switch that controls the flipper is shifted, the sample will be introduced into the settling tube. When the flipper is halfway between the vertical ?????? and contact with the settling tube, move the switch back to its original position. This will prevent the flipper from crashing into the settling tube and introducing noise into the system.

The manual spoon technique simply involves placing the sample split into a tablespoon, dampening the sample with an eyedropper, and dumping the sample in one smooth, rapid motion (from a height of less than 3 cm) down the center of the settling tube.

The operator is encouraged to run a few standards to check for equipment problems and practice sample introduction. This exercise will help the operator to produce more accurate and reproducible analytical results.

After the sample has settled to the bottom of the tube and the pressure differential returns to approximately zero, a hard copy of the sand fraction grain-size distribution can be generated on a strip chart recorder or the terminal (see Figure 4).

14. The fine fraction (silt and clay), which has been stored in Mason Jars of Calgon solution, may be analyzed by pipet or Coulter Counter. The Coulter Counter determines particle volume; the pipet method measures settling rates. The reason for performing the analyses will determine which method will be used (see Comments section, page 36).

The pipet method consists of preparing a dispersed (by sonic probe), homogeneous (by vigorous stirring) suspension of the fine fraction, diluting it with a 0.5 percent Calgon solution to 1,000 ml, and allowing the particles to settle in a graduated cylinder (Folk 1974). The optimum sample is approximately 20 cm^3 (about 15-g dry weight). With more sample, the grains

```
Lab Number AC216
Operator:
Cruise I.D.
Project I.D.
Sample I.D.
Sample weight:    53.8613
Coarse weight:    52.7069
Sand weight:      50.1269
Gravel Fraction Percentages:
-1   Phi % =   28.68
-2   Phi % =   39.92
-3   Phi % =   31.4
-4   Phi % =   0
-5   Phi % =   0
Wednesday 09:32:00 July 25, 1984


PHI           VALUE      PERCENTAGE

-1.5           797        0.000%
-1.0           797        0.000%           0.0%
-0.5           797        0.000%
+0.0           795        0.275%           0.3%
+0.5           794        0.138%
+1.0           774        2.755%           2.9%
+1.5           679       13.085%
+2.0           512       23.003%          36.1%
+2.5           345       23.003%
+3.0           160       25.482%          48.5%
+3.5            79       11.157%
+4.0            73        0.826%          12.2%


Total percentage =  99.8     Remainder percentage =  .199997
Corrected 0 Phi =  .3 %   Corrected 4 Phi =  12.2  %
******************************** PLOT *****************************************
```
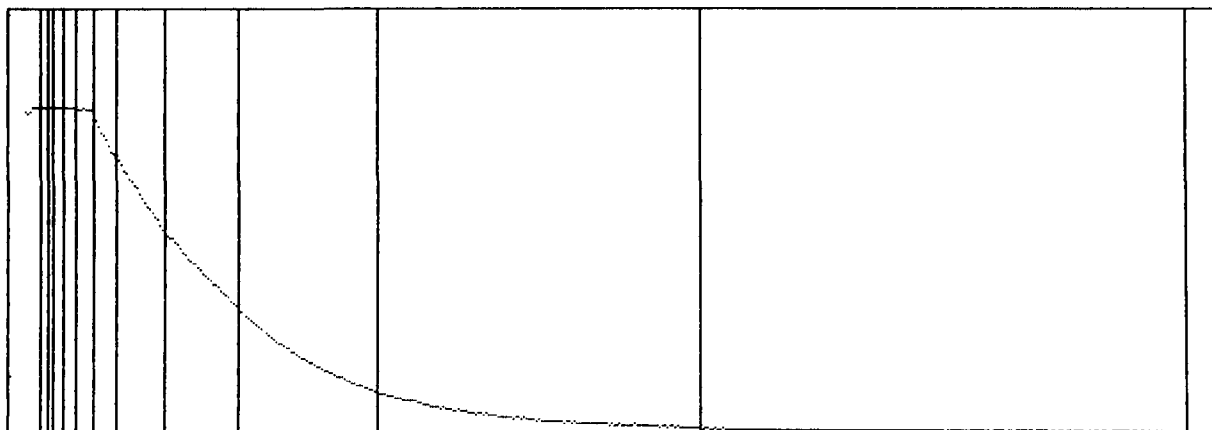

Figure 4. Example of a raw data record produced by an automated settling tube.

interfere with each other during settling; with less sample, the experimental errors in weighing increase with respect to the sample. Withdraw 20 mL samples of the suspension from levels at 5, 10, or 20 cm below the water surface at standard intervals of time (see Table 3). Because all particles of a given equivalent diameter (based on calculations using Stoke's Law) will have settled below that level after a standard interval of time, the samples should contain only finer particles. These aliquots are either suction-mounted on preweighed filters and rinsed in distilled water or placed in preweighed 100 ml beakers. If preweighed beakers are used, the operator must remember to account for the weight of the Calgon when calculating the phi fraction weights. The pipet is rinsed with distilled water after each extraction and the rinse water is also passed through the filter. To begin the analysis, start the timer as soon as tha stirring rod emerges for the last time. At the end of 20 seconds, insert the pipet to a depth of 20 cm and withdraw exactly 20 ml. This is the most important single step, as the subsequent analysis is based on it, so be as accurate as possible. Continue the withdrawals at the specified time intervals and depths. The filters are dried and weighed and the size distribution is calculated from the weight of sediment. The principle behind the computation is this: if the fine sediment is uniformly distributed throughout the entire 1,000 ml column by stirring, and exactly 20 ml is drawn at each of the stated times, then the amount of mud in each withdrawal is equal to 1/50 of the total amount of mud suspended in the column at that given time and at that given depth (i.e., the amount of mud finer than the given diameter; all particles coarser than the given diameter will have settled past the point of withdrawal). The first withdrawal is made so quickly after stirring and at such a depth that particles of all sizes are present in suspension. Therefore, if we multiply the weight of the first withdrawal by 50, we will obtain the weight of the entire amount of mud in the cylinder. If we then withdraw a sample at a settling time corresponding to a diameter of 6 phi, and multiply by 50, we know that the product represents the number of grams of mud still in suspension at this new time: the weight of mud finer than 6 phi. Similiarly we can compute the weight percent at any size and obtain an entire distribution.

Because of the length of time required to complete a whole phi interval analysis (16 hours, 24 minutes to 10 phi at 20 °C) and because Brownian motion interferes with the settling of less than 10-phi-sized particles, the pipet method is now used to determine the silt/clay boundary in percent gravel-sand-silt-clay analyses, and when a sample contains a significant amount of material smaller than 0.4 microns in diameter. This latter condition is important because a Coulter Counter determines a size distribution based solely on the grain-size range it has been calibrated to analyze (typically 0.4 to 62 microns). It is

unfortunate that many low-energy and deep-water environments contain significant amounts of very fine clay and colloidal-sized material that would be ignored by the Coulter Counter.

To perform this silt/clay boundary analysis, collect samples at 20 cm depth after 20 seconds elapsed time to determine the concentration of sample in solution, and at a depth of 10 cm after exactly 2 hours and 3 minutes to determine the concentration of clay-sized (less than 4 microns) material in solution. From the weight of sediment on these filters, the percent silt and clay can be determined.

The time needed to perform a pipet analysis may be reduced by placing the settling cylinders in a constant temperature bath and lowering the viscosity of the settling medium by increasing its temperature (see Part B of Table 3).

TABLE 3. Comparison of withdrawal time and depth tables for temperatures of suspension maintained at 20 oC (Part A) and at 24 oC (Part B)

PART A
****

PHI DIAMETER	WITHDRAWAL DEPTH (cm)	TIME at 20° C
4	20	20 sec.
5	10	1 min., 56 sec.
6	10	7 min., 44 sec.
7	10	31 min.
8	10	2 hr., 3 min.
9	5	4 hr., 6 min.
10	5	16 hr., 24 min.

PART B
****

PHI DIAMETER	WITHDRAWAL DEPTH (cm)	TIME at 24° C
4	20	20 sec.
5	10	1 min., 45 sec.
6	10	6 min., 58 sec.
7	10	28 min.
8	10	1 hr., 51 min.
9	10	7 hr., 24 min.
10	5	14 hr., 50 min.
11	5	59 hr., 20 min.
12	5	237 hr., 20 min.
13	5	949 hr.

****

15. The Coulter Counter is the most widely used particle counter for fine-grained-sediment texture analysis (Fig. 5). It permits easy, fast, and accurate analysis of whole phi grain-size distributions, but, as with any precision instrument, care must be exercised in its use. The instrument's optimum precision, as with all the above analyses, is realized only if the operator is conscientious in attention to detail and consistently follows established procedure. The following procedure is provided because of the general acceptance of the Coulter Counter. It is by no means complete and is intended solely as a set of guidelines. All operators are encouraged to familiarize themselves with the complete Coulter Counter Manual to achieve the best results.

The Coulter Counter is activated according to the following steps: (1) the Coulter Counter and Population Control Accessory are turned on and allowed to warm up for 15 minutes; and (2) a noise check is made using the dummy load.

Place a 200 micron tube on sample stand and turn aperture slightly clockwise; set the Aperture Matching Switch, Size Calibration Channels, and Size Calibration Pot to the proper settings. Set the Gain switch to auto, Active Channel switch to 14-3, Sampling switch to time, Mode switch to volume, and Display Gain switch to X10. Fill a clean beaker with filtered (0.2 micron filter) electrolyte; place the beaker on the sample stand slightly away from the tube with the rubber spatula stirrer centered in the bottom of the beaker; and set the stirring motor to the proper RPM (a high constant speed that does not cause surface turbulence). Check for acceptable cumulative background count: the counts should be less than 500 with the Faraday cage door closed.

Shake the sample in the Mason Jar vigorously and use the whole-sample mixer to completely suspend the sample. While the sample is mixing, use an appropriate pipet to transfer three equal subsamples from the top, middle, and bottom of the Mason Jar to a clean beaker of filtered electrolyte filled to a standard volume (200-300 ml). Never allow the tip of the pipet to touch the side or bottom of the Mason Jar while subsampling. Place the beaker on the sample stand, set stirring motor, and open control stopcock above tube. Open auxiliary stopcock just long enough to clear any bubbles from tube. Push reset button. Bring concentration index meter to a standard 0.03. If the concentration is above 0.03, add more electrolyte to dilute to 0.03. If the concentration is below this, add more subsamples to the beaker until

Figure 5. A Coulter Counter electroresistance multichannel particle size analyzer with the sample stand in a Faraday cage.

0.03 is reached. Check that the concentration is less than the maximum for 5 percent coincidence (less than 10,000 at manometer setting 2.0 CC, 14-3). After pushing reset, wait 5 seconds, then push Accumulate. When the calibration light comes on, push Stop and close the tube stopcock. If the system is computer automated, record the data from each channel to disk while the Scope Display switch reads differential percent. This is accomplished by pressing the Print/Plot button with the Print/Plot switch set to interface. If the system is not automated, the printer in the Population Control Accessory (PCA) should be used to generate a hard-copy by pressing the Print-Plot button with the Print/Plot switch set to print. The operator should periodically check to be sure that the PCA data match the LED readout. Remove the beaker from the sample stand, cover it with cellophane to avoid contamination, and reserve the sample for the 30 micron tube analysis. Complete only enough 200 micron analyses to permit adequate time in which to perform the 30 micron analyses on the same day.

Change to 30 micron tube; set Aperture Matching switch, Size Calibration pot, Active Channel switch, Gain Control, and Channel Selector switch to the proper settings. Place a clean beaker of electrolyte on the sample stand and check for acceptable cumulative background count. Do not use the stirrer motor during 30 micron tube analyses. Pour the sample saved from 200 micron analysis through a clean 20 micron micromesh sieve into a clean electrolyte-rinsed beaker. Immediately place beaker on the sample stand and open tube stopcock; open auxiliary stopcock to clear bubbles from tube, and then push reset. Push Accumulate button and stop when the calibration light comes on. Record the data from each channel to the computer disk. If a computer will not be used to integrate the 200 and 30 micron data sets, switch the gain control to Manual and match the differential percent from channel 12 or 13 with the differential percent from channel 5 of the 200 micron tube analysis. Record the differential percentiles and manually normalize the results.

NOTES:
* Always keep Faraday cage door closed during analyses.
* Make sure bubbles are cleared from tube aperture by opening both stopcocks.
* If the tube clogs, brush the aperture opening. If the tube is still clogged, clear tube in a distilled-water ultrasonic bath. If this fails, replace the distilled water with 50 percent nitric acid.

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* Always have aperture current in OFF position when not running an analysis.
* Check AGC card weekly.
* After the analyses are completed, the sample stand, Faraday cage, vacuum and electrolyte reservoir flasks, and counter top should be rinsed in distilled water and dried with paper towels.
* When the analyses are complete remove the 30 micron tube, place the 200 micron tube on the sample stand, and set all switches to the proper settings for a 200 micron analysis.

16. There are innumerable ways to present the results of textural analyses. The technician may compute the modified frequency percentage; method of moment statistics; percentages of gravel (greater than 2.0 mm), sand (greater than 63 microns and up to 2 mm), silt (greater than 4 microns and up to 63 microns), and clay (less than 4 microns); and the modified frequency percentages for size distributions up to and including 11 phi to -5 phi (0.4 microns to 64 mm). The method of moments statistics generated often include modal classes and frequencies; arithmetic mean, median, and standard deviation; skewness; and kurtosis. A histogram, a cumulative frequency plot, inclusive graphics statistics (Folk 1974), and verbal equivalents for standard deviation, skewness, and kurtosis may also be produced.

Because the most effective way to describe and summarize a set of numbers is to visually inspect pictures of these numbers, data graphics should do more than simply substitute for statistical tables. They should convey both quantitative and categorical information and allow the viewer to decode the portrayed data with precision and efficiency. To do this, choose graphical methods in textural analysis depending on whether you are comparing changes (1) within a given sample, (2) within a sedment core, or (3) between samples at one or more geographic sites.

Histograms and cumulative frequency curves efficiently show the size distribution with a given sample. A histogram is essentially a bar graph in which the percentages for each size grade (usually a whole phi interval) are plotted as columns (Fig. 6). The histogram is useful as a pictorial method to show sorting and modality but cannot be used to readily determine any statistical parameters such as the median or graphic mean. The arithmatic ordinate, cumulative frequency curve is the most commonly used graphical method for portraying the grain-size distribution within a given sample (Fig. 7). The advantage of this method is that all statistical parameters (median, mean, standard deviation, skewness, etc.) may be calculated directly from the curve allowing quantitative comparison between samples.
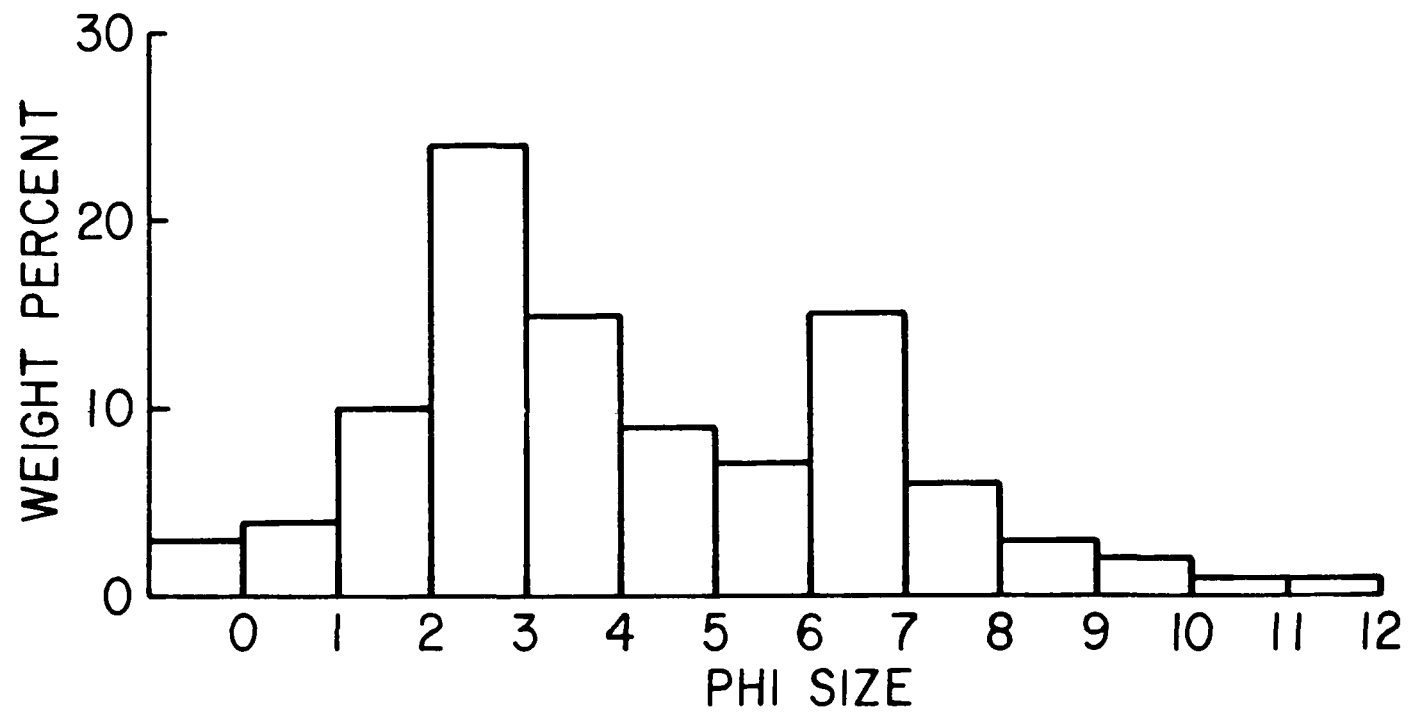
Figure 6. Histogram of a bimodal, poorly sorted, silty sand.
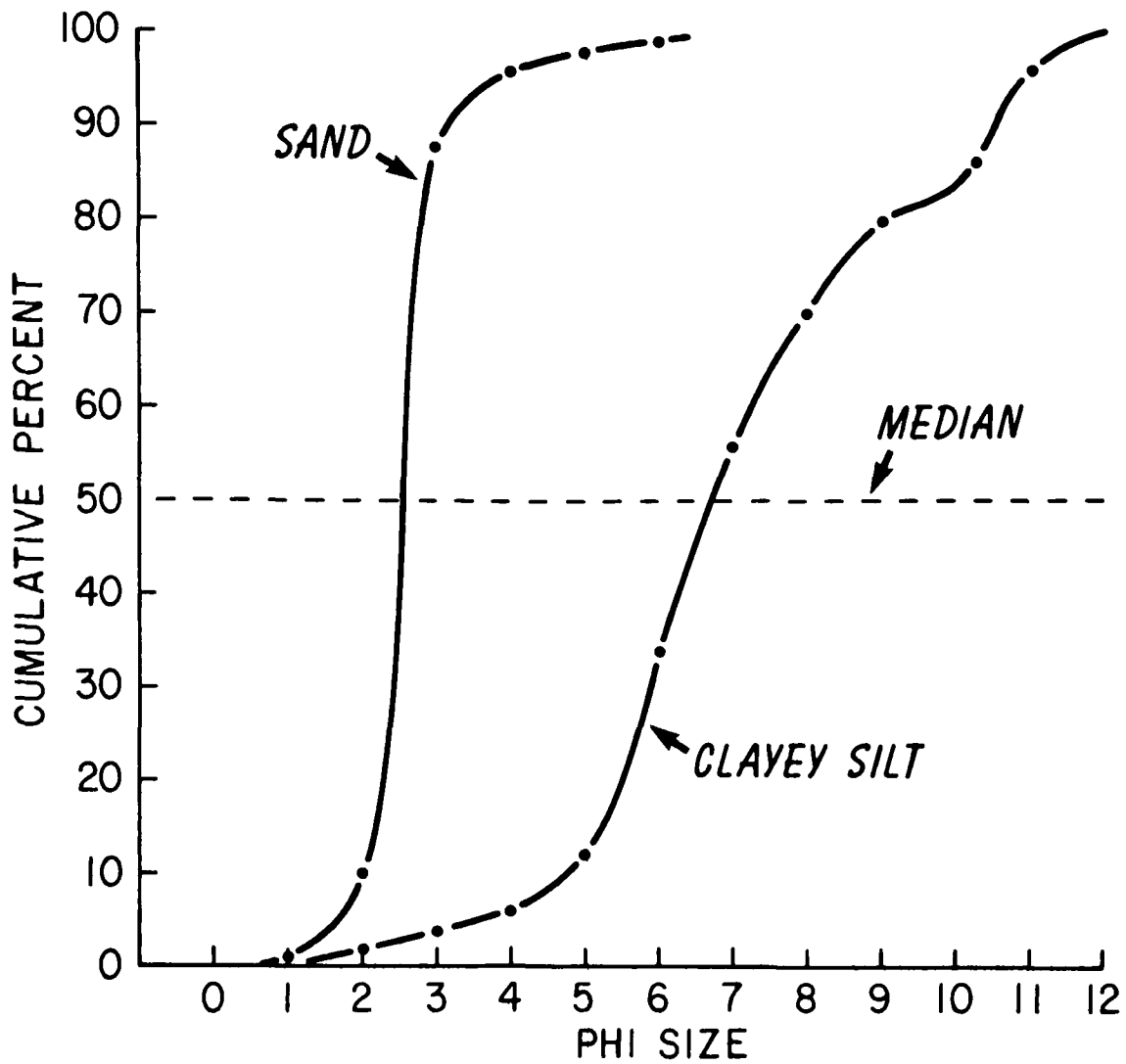
Figure 7. Arithmatic ordinate, cumulative frequency curve of a well sorted, unimodal sand and a very poorly sorted, bimodal clayey silt.

Moving-average plots are commonly used to show particle size variation with depth in a sediment core (Fig. 8). The advantages of these plots are that they are very pictorial, combine the data from any number of samples, and distinctly show gradual and abrupt changes in sediment texture; the disadvantage with these plots is that the only quantitative information conveyed is relative percentages among the gravel, sand, silt, and clay fractions.

The triangular diagram (Shepard 1954) is recommended for graphically comparing sample variations within and between sets of textural data. In a triangular diagram, an equilateral triangle is divided into smaller triangles as shown in Figure 9. It allows expression of the texture fractions of a sediment in terms of three components, sand at the apex, silt at the left-hand corner, and clay at the right-hand corner. A three-dimensional diagram; i.e., a pyramid, permits plotting four components, for instance a gravel in addition to the other three size fractions. The advantage of the triangular diagram is that more than one sample, and for that matter more than one group of samples, may be readily compared using one diagram. The disadvantage of the traingular diagram, like that of the moving average plot, is that the only quantitative information conveyed is relative percentages among the sand, silt, clay, and perhaps gravel fractions.

Comments

The purpose of the analyses must be considered when selecting which method will be used. For example, the Coulter Counter determines particle volume, as opposed to the pipet method, which measures settling rates. Therefore, if a researcher is studying flow regimes and hydraulic equivalents, the pipet method might produce more applicable data. Other settling-velocity analysis methods used for fine-grain sizes are the hydrometer (Buoyocoz 1928) and decantation methods. However, these techniques are more difficult and less accurate (Folk 1974) and thus are generally not recommended. Numerous journal articles have compared the various techniques used for size analyses of fine-grained suspended sediments. All operators contemplating the use of any of these methods are strongly encouraged to familiarize themselves with this literature. For example, Shideler (1976) and Behrens (1978) compared the Coulter Counter with pipet techniques. Hydrophotometers have been compared with the pipet method by Jordan and others (1971) and with the Coulter Counter by Swift and others (1972).

The fine-fraction considerations also apply to the coarse fraction. The coarse fraction is usually determined by settling-tube analysis. However, if this fraction weighs less than 5 g or contains greater than 5 percent foraminifera, which will not settle properly in a sedimentation column, the operator must utilize sieves to measure nominal diameter. Barth (1984) discusses these and other particle-size methods and considerations.

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Figure 8. Moving average plot of a core penetrating interbedded silty sands and clayey silts.
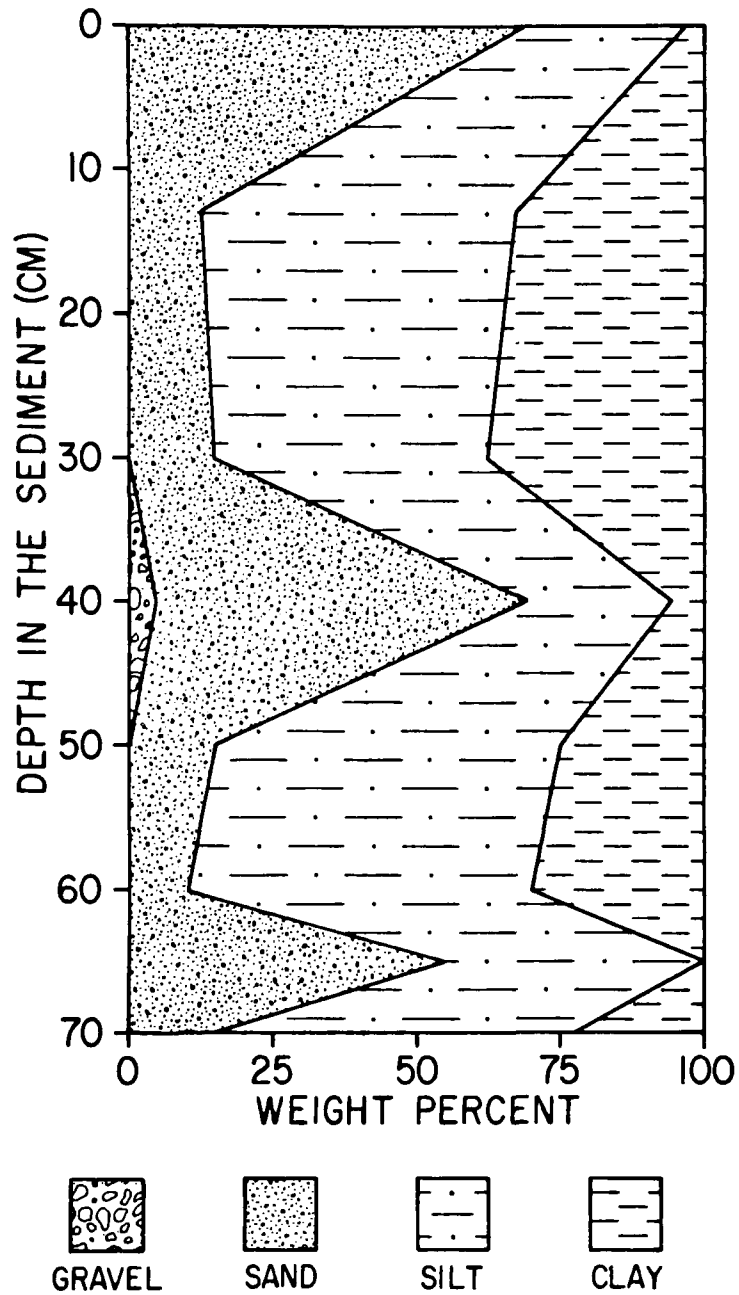
Figure 9. Graphical representation by a triangular diagram. Solid square represents a silty sand composed of 65% sand, 25% silt, and 10% clay; solid circle represents a sandy silt composed of 35% sand, 60% silt, and 5% clay; and a solid triangle showing a silty clay composed of 15% sand, 40% silt, and 45% clay.
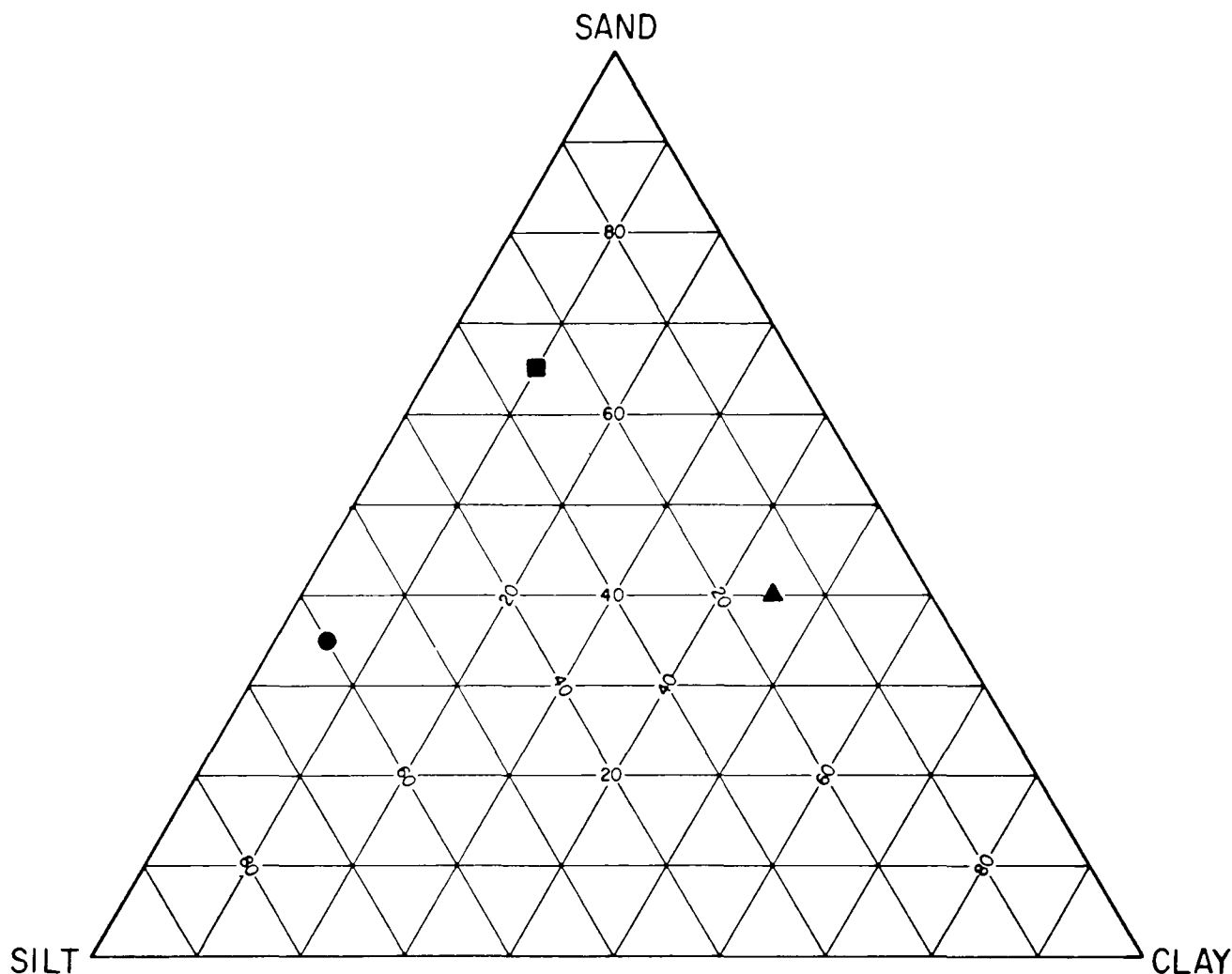
Quality Assurance

Extensive textural analysis performed on standards have shown that the above methods, with the possible exception of the hydrometer, will produce results with an accuracy of better than plus or minus 10 percent (particle counter, 3 percent; sieves, 5 percent; pipet and sand-fraction settling tube, 5 percent). However, optimum precision for these is realized only if the operator is conscientious in attention to detail and consistently follows established procedure. To monitor precision, the operator should run replicates on at least every tenth sample.

As discussed earlier, the representativeness of any grain-size distribution data set depends on the methods used to obtain the data. These methods must be chosen in accordance with the original purpose of the study. If it is more important to know the actual size distribution than to know the hydraulic equivalence, the sieve and the particle-counter analyses should be performed rather than the settling-tube and pipet analyses.

The comparability problems between sets of data generated by different devices are not as great as one might expect. For example, the data produced by sieve and settling tube analyses would be remarkably similar for a given sample because a settling tube is usually calibrated using natural sediments sieved to known fractions. On the other hand, pipet and hydrometer analyses will usually produce data indicating a given sample is slightly finer than will the data produced on a Coulter Counter or the equivalent. This result occurs because fine-fraction particles are generally plate shaped and do not settle as fast as the quartz spheres upon which Stoke's Law, and therefore the pipet and hydrometer settling analyses, is based. Also, a Coulter Counter typically cannot be calibrated to analyze the very fine clay (less than 0.4 microns) and colloidal portions of the size distribution.

Cost Analysis

Cost estimates are based on complete analyses (including -5 to 11 phi size distribution; percents gravel, sand, silt, and clay; statistics; histogram and cumulative frequency plots; and verbal equivalents) performed on an automated system. Production rate is 25 samples/week. The ranges in labor, and therefore, total cost are dependent on the salary of the employee who actually performs the analyses. The estimates shown in Table 4 assume typical salary levels for a technician, a supervisory scientist, and the cost of using a Coulter Counter.

When other techniques are substituted, the cost/sample changes. When sieves are used instead of the settling tube, the cost/sample increases by $4/sample because of the increased time

spent running the Ro-tap, weighing the phi fractions, and manually entering the data into the computer. Similarly, utilizing a pipet rather than the Coulter Counter would vastly increase the cost because of the extended analysis time. Inasmuch as no more than six or seven samples can be run concurrently because of the frequency and resultant interference of sampling times, it would take 16 to 17 hours to run six samples at room temperature (about 20° C) or 8-9 hours to run six samples using a constant temperature bath (about 32° C). These settling analyses add about three days, plus 24 hours of overtime in the case of the room temperature scenario, to the time it takes to perform 25 analyses; in this case, the technician cost/sample total would increase by $7 to $17. All cost estimates are based on the use of an automated data-reduction system. If the calculations necessary to normalize and combine the coarse and finefraction distributions and generate the statistics are performed by hand, the labor cost/sample would increase by about $21/sample.

All estimates are based on the analyses being performed at a functioning sedimentation laboratory.

TABLE 4. Cost per sample estimates for a typical computerized sedimentation laboratory.

Labor	$ 20 to $35
Equipment depreciation, maintenance and expendable materials	$ 5
Overhead and Contingencies	$ 20 to $30
Total 1. Coulter/settling tube	$ 45
2. Coulter/sieve	$ 50
3. Pipet/settling tube	$ 65
4. Pipet/sieve	$ 70
COST PER ANALYSIS AT BATCH RATE	$ 70

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CHAPTER 4

X-RAY DIFFRACTION MINERALOGY

Introduction

The petrographic examination of sediments by means of an optical microscope is generally more accurate than X-ray powder diffraction analysis for the sand-sized fraction, and gives information on the genetic relationships and associations of the minerals as well. However, quantitative analysis of silt-sized particles by petrographic microscope is time consuming and difficult, and is often almost impossible for clay-sized material. Because of this, X-ray powder diffraction has become a common tool for mineralogic investigations during the last four dacades.

Procedure

A split from each sediment sample is dried at 60° C, mounted, and X-rayed as a randomly oriented powder (Appendix A). The random orientation insures that the incident x-rays have an equal chance of diffracting off the crystal lattice face of any given mineral present in the sample. The use of a powder press to make randomly oriented powder mounts is undesirable because excessive force could cause preferred orientation of the crystallite. The randomly oriented mounts are X-rayed between the angles of 2° and 70° 20' using CuKo radiation and a scanning rate of 2°/minute. Slower scanning rates substantially increase analysis time and are usually not necessary if long-fine-focus or fine-focus X-ray tubes are used.

The clay fraction from each sample split used in a randomly oriented aggregate is separated by centrifuge (Appendix B) and mounted as an oriented aggregate mount on a silver membrane filter (Appendix C). These oriented aggregate mounts force the clay minerals, usually plate-shaped phyllosilicates (layer-silicates), to lie flat, allowing the operator to direct the incident X-ray beam down the c-axis of these minerals. It is the c-axis that shows the extent of d-spacing expansion and/or contraction indicative of certain clay minerals during the subsequent treatments. Silver membrane filters can be used as substrates for oriented clay samples because they are not affected by heat or organic solvent treatments and because they can be prepared rapidly and easily using readily available laboratory equipment.

Each oriented aggregate mount is subjected to four treatments to determine which clay minerals are present: air drying, glycolation with ethylene glycol (Appendix D), heating to 400° C (Appendix E), and heating to 550° C. After each

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treatment the samples are X-rayed between the angles of 2° and 40° 20'. The individual clay mineral species are then identified using the flow charts presented in Appendix F.

Mineral identification is useful only if some quantitative distinction between the mineralogy of different samples can be made. Truly quantitative evaluations are not yet possible in complex mineral assemblages, but by utilizing the areas and intensities of characteristic X-ray peaks, useful semiquantitative approximations can be found. The intensity of a mineral's characteristic X-ray diffraction peaks cannot be used as a sole measure of its abundance because of the variations between diffraction patterns that are caused by X-ray machine conditions and by differences in sample thickness and the degree of preferred orientation. In addition, different minerals, different atomic planes within a mineral, and different samples of the same mineral generally do not have the same capability to diffract X-rays. Other complications arise from sample dilution by amorphous phases invisible during X-ray diffraction analysis; a marine sample, for example, may contain a significant siliceous microfossil component.

However, many semiquantitative methods exist and are commonly used. The basic principle is that weight fractions can be calculated from the peak areas and intensities, mass absorption coefficients, densities, and constants. Some of the more common methods are: spiking/dilution, internal standard (as described by Klug and Alexander 1954), standardless (Zevin 1977), external standard (Copeland and Bragg 1958, Geohner 1982 and Pawloski 1985), and matrix flushing (Chung 1974). An adaptation of the external standard method is usually preferred. In this method, semiquantitative estimates of the minerals present in the randomly oriented mounts are made by comparing at least three diffraction maxima intensities and areas for each mineral within a sample, with the areas and intensities recorded from a collection of standards. Only peaks that do not represent over-lapping diffraction maxima are chosen for the comparison. The collection of standards should be extensive and consists of both monomineralic and multiphase X-ray patterns. These patterns can be generated from mineral samples purchased through any of the scientific supply companies. A quartz standard is run daily to monitor keV and mA drift, long term drift of the X-ray tube (aging), and alignment problems, such as sample positioning in the goniometer circle and slight goniometer alignment changes. Changes in the quartz standard pattern are factored into the collection of mineral standards. The relative percent of the clay-mineral sample is estimated from the intensity and area of the 4.5 angstrom peak, which is common to most clay minerals in randomly oriented powder mounts.

During clay mineral analyses, useful comparisons may be made from sample to sample by means of various ratios of peak

areas. Relative percentages among the clay minerals are estimated by a method adapted from Biscaye (1965). The method calculates weighted peak area percentages for smectite, illite/mica, kaolinite, chlorite, and mixed-layer smectites. The peaks and weighting factors used are: (1) the area of the 17-angstrom glycolated peak for smectite; (2) four times the 10-angstrom peak area for illite/mica; and (3) twice the area of the 7-angstrom peak for the combined total of kaolinite and chlorite. Individual kaolinite and chlorite percents are assigned according to the ratio of the 3.58-angstrom kaolinite and 3.54-angstrom chlorite peaks. The weighting factor for smectite adjusted for the amount of illite layers or chlorite layers present in the crystal structure is used to calculate the semiquantitative estimates for the mixed-layer smectites. All peak areas are generally computed from the glycolated pattern.

The term illite/mica is used to refer to all 10-angstrom minerals, except glauconite, which do not swell upon glycolation and which are not destroyed when heated to 550° C. This term is necessary because it is often difficult to distinguish between the various minerals that show 10-angstrom reflections (such as muscovite, biotite, sericite, lepidolite, illite, and phlogopite) in normal diffraction analyses. The term smectite is used to describe a group of swelling minerals that are represented principally by montmorillonite, beidellite, nontronite, saponite, hectorite, and sauconite. If necessary, the individual illite/mica and smectite minerals may be differentiated by a combination of diffraction and geochemical techniques. For example, some of the illite/mica minerals and their polymorphs may be distinguished by the location of the 060-hkl diffractions, and montmorillonite and beidellite can be differentiated by lithium saturation (Schultz 1969).

A split is taken from each sample and mounted in artificial Canada balsam (such as Piccolite or Caedex) as a smear slide (Appendix G). These slides are used to check the semiquantitative diffraction techniques, to detect amorphous materials or material present in trace amounts, to detect layer-silicate species concentrated in the sift fraction, and to examine the biological debris. When these semiquantitative estimates are made in conjunction with smear slides, the estimates are generally considered to be accurate to within 10 percent of their actual values; however, the smaller values may vary by considerably more than this.

Comments

Silver membrane filters can be used as substrates for oriented clay samples because they are not affected by heat or

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organic solvent treatments; they can be prepared rapidly and easily using readily available laboratory equipment. The silver of the substrates gives no maxima at diffraction angles less than about 30° 20' using copper radiation. This contrasts with glass (Croudace and Robinson 1983, Drevey 1973 and Pollastro 1982), plastic-filter, or ceramic-tile substrates (Shaw 1965), which produce significant amorphous or crystalline diffraction effects between about 10° and 30° 20' and errors due to segragation (Gibbs 1965). The high mass-absorption coefficient of silver to copper radiation results in a lower overall background than these other materials, but does not decrease diffraction intensitites produced by the sample; the silver underlies, but is not mixed with the sample.

Poppe and Hathaway (1979) have developed a method for mounting silver substrates (Fig. 10) that permits easy installation and removal of silver filters, presents a flat, even sample surface in the correct position relative to the X-ray beam, and fits automatic sample changers. Other silver filter mounting methods include glued mounts, vacuum mounts, and top clamp mounts. Each of these last techniques has significant disadvantages. The glued mount is inconvenient and often leaves the sample in a condition in which further treatments that are important in the identification of clay minerals cannot be made. If separate mounts are prepared, the differences in sample thickness retained on each silver filter result in faulty surface positions. Also, duplicate filters may show variations in preferred orientation and thus give different diffraction intensities. The vacuum mount is unacceptable because it can be adapted to an automatic sample changer only with great complexity. A mount in which the filter is held in place by clamps on the top of the mount likewise will not consistently reproduce an even sample surface, the vertical position of the sample is highly variable, and the clamps tend to produce diffraction and fluorescence effects at low goniometer angles.

An adaption of the external standard technique is preferred. There are several important advantages to using this peak area and intensity ratio technique as a semiquantitative method: sample preparation time is minimal; the randomly oriented aggregate mount need be X-rayed only once; and patterns are generated in a reasonably short period of time (35 min.).

Internal standard methods, such as spiking/dilution, generally require more time in which to prepare the samples and calculate the results than do external standard methods. The standardless technique involves complicated calculations and has a greater inherent error than the internal or external standard methods. Matrix flushing, which also involves complicated

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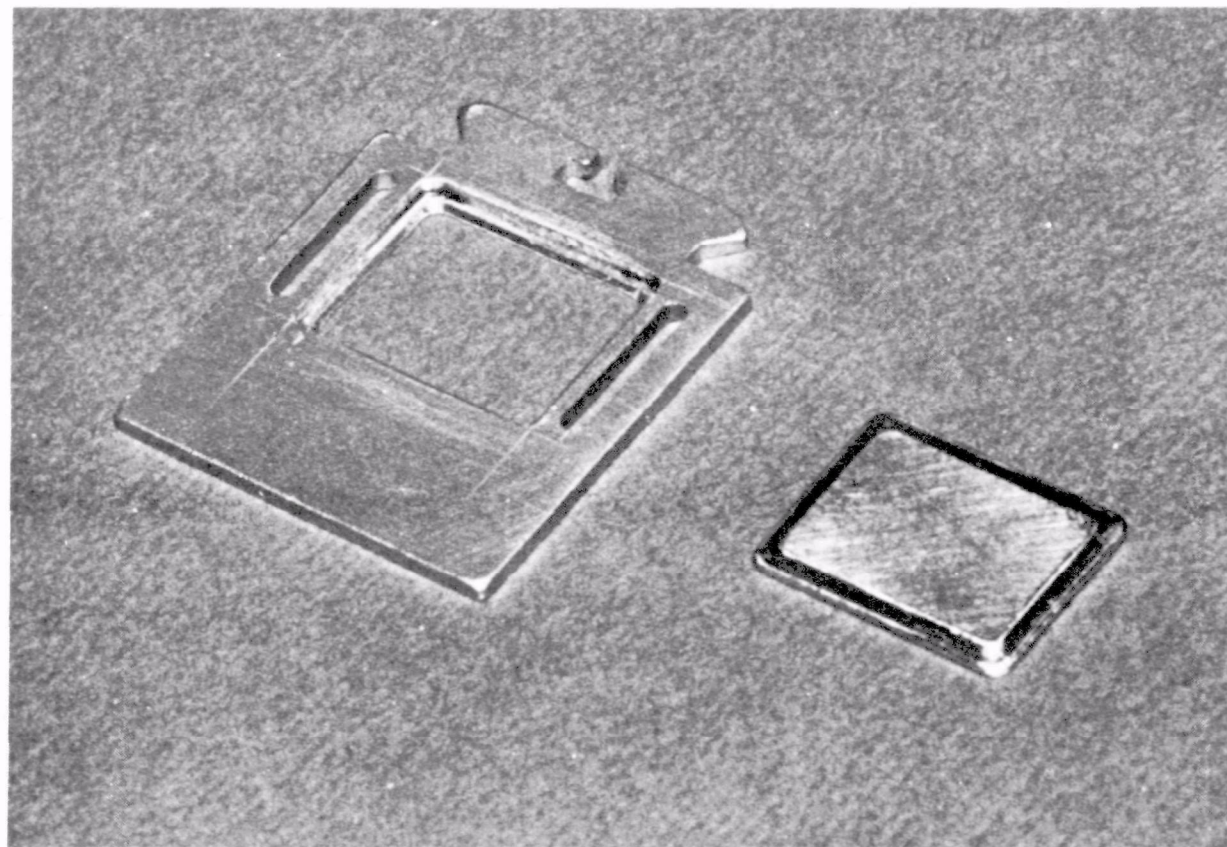
Figure 10. A metal membrane mount used for X-ray powder diffraction.

calculations and increased time for sample preparation, is applicable mainly for differentiating polymorphs and solid solutions.

Satisfactory estimates of silica (opal) concentrations may be made from this area of the 4.10-angstrom peak or from a technique described by Goldberg (1958). It is sometimes desirable to analyze the mineral suite of a more limited grain-size fraction. When this is done, the sand, silt, and clay fractions may be separated by sieve and settling techniques and each fraction may be independently subjected to x-ray diffraction and microscopic analyses.

Quality Assurance

The accuracy of any measurement is limited by the capability of the operator, the sampling (see Chapter 2) and measuring techniques, and the equipment. Semiquantitative X-ray diffraction analyses of multiphase mineralic knowns have shown that when the external standard method is used in conjunction with an extensive mineral reference library, it will produce results with an accuracy of better than +/- 10 percent of the amount present. However, the accuracy decreases (owing to the counting statistics, if nothing else) with the amount of a mineral present. At a 1 percent true concentration, an estimate may be off by a few hundred percent of its true concentration, resulting in an estimate of 2 or 3 percent. The optimum precision is realized only if the operator is conscientious in attention to detail and consistently follows established procedure. To monitor accuracy and precision, the operator must analyze a standard (such as quartz) daily, occasionally rerun other monomineralogic and multiphase standards, and run replicates on at least every tenth sample.

Because semiquantitative results are only as good as the strip chart trace of the X-ray diffraction pattern, care must be taken when comparing semiquantitative X-ray analysis data sets that have been generated using different sample preparation techniques. For example, any method that requires gravitational settling of the suspended clay fraction onto a glass slide or ceramic tile, or one that does not instruct the technician to grind the entire sample to less than 62 microns for the randomly oriented mount, may cause partitioning within the sample and prevent an accurate representation. For randomly oriented powder sample preparation, a free-falling method such as the technique described by National Bureau of Standards Monograph 25 (1971), shown in Appendix A, is recommended to avoid the preferred orientation often associated with other packed powder methods.

Cost Analysis

Cost estimates are based on a complete analysis (randomly oriented and oriented aggregate mounts and smear slides). Production rate is typically 25 samples per week. Cost per sample totals (Table 5) are given in ranges; exact costs would be determined by the number of samples contracted. Labor costs, and thus total costs, would vary according to the salary of the employee who actually performs the analyses. Accordingly, representative salaries for a technician and a supervisory scientist have been factored into the estimate.

The use of glass slides as substrates for randomly oriented mounts or as filter peel substrates for oriented aggregate mounts would lower the expendable materials cost by $1 to $1.50 per sample. It would also, however, raise the labor cost because the automatic sample changer could not be used. This would require that a technician monitor the diffraction unit instead of simultaneously working on a different phase of the analysis. This could also limit operation of the diffractometer to business hours and thus increase the cost per sample by $3.50 to $7.00.

The semiquantitative method chosen also affects the total cost. The external-standard, spiking/dilution, and internal-standard methods all require the use of a mineralogic reference library, but the spiking/dilution and internal-standard methods require more time for sample preparation and data processing, resulting in a $3.50 to $8.00 cost increase per sample. The standardless method would lower the cost per sample slightly, despite the time needed for complicated calculations that require extensive programming, because it eliminates the need for an extensive reference library. Unfortunately, it is the least accurate of the semiquantitative methods.

Numerous special techniques, such as the differentiation of the individual illite/mica or smectite group minerals, are used for specific research problems. These techniques invariably increase the expendable materials and/or analysis time costs and, therefore, the cost per sample. All estimates are based on the assumption that analyses are performed at a functioning X-ray diffraction laboratory.

TABLE 5. Breakdown of analysis costs for semiquantitative estimates of mineralogical composition using X-ray powder diffraction.

Labor	$ 25
Equipment depreciation, maintenance, and expendable materials	$ 15
Cost of Overhead and Contingencies	$ 35
COST PER SAMPLE AT BATCH RATE $75	

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CHAPTER 5

RADIOGRAPHY

Introduction

Radiographing cores of unconsolidated sediment allows the nondestructive observation of certain textural and structural features of the sediment by revealing density contrasts. This "internal" view has proved invaluable in the study of marine sediment because many of the relevant facts shown on the radiograph are often obscured to the unaided eye. Features such as laminae, clasts, changes in grain size, burrows, and shell fragments are commonly observed in x-radiographs; and in some cases, the degree of bioturbation can be estimated.

X-rays pass through limited masses of solid matter (e.g., sediment) and strike x-ray sensitive film, where the differential absorption of X-rays -- which is caused by different densities within the sediment -- is recorded.

The energy of the X-ray produced by the X-ray tube is expressed as units of kilovolts potential (kvp). X-rays that have greater energy (harder X-rays) have a shorter wavelength and are capable of greater penetration. A radiograph produced with hard X-rays will have relatively little contrast compared to one made with less energetic X-rays. Choice of energy is often a matter of experimentation and depends on the thickness of the sample, its density, and on its composition. For example, sediment with a high calcium content will require greater energies for proper exposures.

Resolution of detail and contrast in the radiograph are controlled by the energy of the X-ray, the type of film used, the exposure time, and the number of X-rays produced by the source (Haublin 1971).

A variety of X-ray sensitive films is available, but for sediment radiography, a fine-grained film that provides high contrast is desirable. A typical industrial x-ray film that meets this criterion is Dupont Cronex NDT55. Film should be used without lead screen in pack, a common practice in industrial radiography.

The intensity of the beam of X-rays governs the exposure time. For example, if a good exposure was obtained at 4 mA for 2 min. an exposure of equivalent quality would be produced at 1 mA for 8 min. Intensity is also a function of the distance of the source to the plane of the film, as X-rays follow the inverse square law.

The equipment and facility must meet the various safety requirements for users of X-rays. Proper shielding and remote control of the X-ray unit are crucial.

Procedure

Most industrial or medical x-ray generating units can be used for sediment radiography. Typically these units can (1) generate energies of up to 150 kvp (which may be required for thick samples), although 100 kvp is generally adequate; (2) develop intensities greater than 8 mA; (3) accomodate samples longer than 30 cm (the minimum length of cores for site monitoring); and, (4) permit the samples in both vertical and horizontal orientations.

Because sediment cores are typically cylindrical, a radiograph that properly exposes the center of the core will overexpose its edges. To eliminate this effect, use a plexiglass box that is just large enough to hold the core. With the core in the box, the remaining space can be filled with a very fine grained powder that closely matches the composition of the core. Powdered clay-mineral products such as a drilling mud or a beneficiated bentonite product of Georgia Kaolin Company (Elizabeth, NJ) or Englehart Industries (Carteret, NJ) have been used successfully. This combination provides a consistent thickness of material through which X-rays pass, giving a more uniform exposure.

The core to be radiographed should not be frozen because ice crystals may show in the radiograph. If possible, water should be drained from the core to produce a sharper image (it may be worthwhile to collect an additional core or subcore if drainage seems necessary). Place the core in the plexiglass box, then fill the box with clay, making sure there are no voids. Position the box directly in front of the X-ray tube aperture. The sample should be a distance of about 1 m from the X-ray source. The film packet can be taped directly to the back of the box. Small lead letters can be taped directly to the front of the film packet, identifying the sample and providing orientation of the radiograph.

Considerable trial and error is often required to obtain the optimum combination of voltage, amperage, and exposure time needed to produce the best radiograph. If experimentation is needed, begin by using the lowest energy (kvp) possible because this enhances contrast relative to the "harder" X rays. As a frame of reference, the following data are provided: the subject is a 6.5-cm diameter core, containing overlying water, positioned in a plexiglass box full of powdered clay.

Amperage:	6 mA
Voltage:	130 kvp

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Time:                           3 min
Film:                           Dupont Cronex NDT-55
Distance:                       42 in
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Details on exposure are available from film manufacturers. Film should be developed as the manufacturer specifies. Make sure that the developer and other chemicals are fresh or replenished. If an automatic developing system is used, be sure that all rollers have been thoroughly cleaned before beginning. Poor developing technique can cause mottling of the radiograph.

Interpretation of radiographs is qualitative, but radiography does allow observation of many sedimentological features that are not visible normally. A useful overview of radiograph interpretation is given by Bouma (1964). When concerned with biogenic structures, interpretations from paleontology often are helpful (Seilacher 1964). Interpretations of primary sedimentary structures that can be observed in radiographs are given in Middleton (1965).

Comments

If keeping a core specimen intact is unncessary and the sediment is relatively firm, the core can be split lengthwise or cut into tabular sections ("slabs") a few centimeters thick. Preparing the sample in such a manner often results in a radiograph that shows more detail and can eliminate the need for clay fill around the core.

Longer radiographs can be produced if the x-ray head or the core is mounted on a track. This configuration permits a flow-type print to be produced, and may eliminate the need to section cores.

Radiographs have been successfully taken at sea. This capability can provide valuable site information while in the field and help evaluate core quality as well.

Quality Assurance

Judging the quality of radiographs is subjective and, because the procedure is nondestructive, the number of attempts required to produce a suitable product is largely up to the investigator. There are, therefore, no standards or established criteria for evaluation of the product.

Cost Analysis

Time required for analysis   8 hours

    COST PER RADIOGRAPH AT BATCH RATE $ 300

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GEOCHEMICAL METHODS

CHAPTER 6

DISTRIBUTION RATIOS (R_d)

Introduction

The distribution coefficient is a measure of sorptive behavior that is useful in characterizing transport of radionuclides between bottom sediments and overlying fluids in natural water bodies (Pietrzak and others 1981). It estimates the partitioning coefficient between ions associated with solid particles in a porous medium (sediments) and the same ions associated with the liquid phase, based largely on surface adsorption. It will yield useful comparative information primarily for ions of type A in Table 6. These are ions that are relatively insensitive to oxidation/reduction conditions in the sediment, and are most likely to behave similarly under both field and laboratory conditions.

The method is a short-term batch sorption technique based on recommendations in Relyea (1980). Results are described in terms of R_d, the distribution ratio, or apparent distribution coefficient, rather than the distribution coefficient (K_d). The use of K_d implies presence of chemical equilibrium, which may not be present, and/or may be difficult to document in the natural systems in question. To the maximum extent possible, the test should bracket certain parameters of the actual disposal environment, such as solution concentrations, temperature, and pH.

The distribution ratio (R_d) for a specific chemical species is defined as:

$$R_d = C_s/C_l, \quad \text{where}$$

C_s = mass of solute on the solid phase per unit mass of solid phase, and

C_l = mass of solute in solution per unit volume of liquid phase.

For radioactive species, C_s equals the activity of solute on the solid phase per unit mass of solid phase, and C_l equals the activity of solute in solution per unit volume of liquid phase. R_d is often expressed in units of milliliters of solution per gram of solid (sediment) under steady-state conditions. These conditions are defined here as meaning that R_d values obtained for three separate samples of sediment exposed to the contact liquid for 3 to 14 days shall not differ by more than the expected precision, other conditions remaining constant. R_d and K_d are defined identically under equilibrium conditions; i.e., $K_d = R_d$.

Table 6. Selected radionuclides (beta and gamma emitters) potentially associated with nuclear reactor waste (partly from Bowen 1979 and Burman 1986).

Isotope	T 1/2 (yr)	Category	Typical Redox Reactions
Ag-110	0.69	D	S
Am-241	433	A	RE analog
Co-60	5.1	C-D	Co (II-III), S
Ce-Pr-144	0.78	C	Ce (III-IV)
Cs-134	2.1	A	
Cs-137	30	A	
Cm-243	32	A	RE analog
Eu-155	4.9	C	Eu (II-III)
Fe-55	2.7	C	Fe (II-III), S
H-3	12.3	A	
I-129	16.0×10^6	B	$I^- - IO_4^-$, organics
I-131	0.022	B	$I^- - IO_4^-$, organics
Kr-85	10.3	G	
Nb-95	0.1	C	Nb (IV-VI)
P-32	0.04	A	PO_4^-, organics
Pm-147	2.6	A	RE analog
Pu-239	24,100	C	Pu (III-IV-V-VI)
Pu-240	6,570	C	Pu (III-IV-V-VI)
Ru-106	1	A	
Sb-125	2.7	C	Sb (III-V), S, H
Sm-151	90	A	RE
Sr-Y-90	28.8	A	
Tc-99	2.1×10^{-5}	C	Tc (II-IV-VII)
Zn-65	0.67	D	S
Zr-95	0.18	A	

Key to Table

A = elements relatively unaffected by redox reactions
B = halogens (iodine)
C = transition and redox-active metals
D = heavy metals not directly subject to common reduction
        processes, but subject to precipitation or complexation
        by sulfide or other reduced phases
G = gas phase

T 1/2 = the half-life of each isotope listed (in years)

RE = rare earth
S = sulfide
H = an organic biomethyl group-former.

Procedure

R_d analysis should begin with samples that are fully representative of the in-place sediments, including both organic and inorganic components where the former are significant. Care should be taken to preserve natural moisture content and, whenever possible, the experiments should be conducted as soon as possible after sediment recovery. This will minimize, but not eliminate, phase changes that may occur during storage, such as reduction of iron oxides, reduction of pore water sulfates to hydrogen sulfide with ensuing precipitation of metal sulfides, or oxidation of naturally occurring sulfides to sulfuric acid. Freezing in sealed plastic containers that allow for expansion room is considered optimal storage; if this cannot be done, sealed storage at 4 $^{\circ}$C is preferred to room temperature storage.

Effective diffusion coefficients for dissolved ions in the sediments must be known as well as R_d values before prediction of radionuclide transport can be attempted. Other background information, including mineralogy, solid-phase chemistry with special emphasis on Fe and Mn concentration, and geochemical environment, possibly including pore water chemistry, is recommended to be conducted. The specific parameters that are most important will vary with each radionuclide.

To assess the effect of organic matter on the R_d values, you may have to perform parallel measurements of R_d on representative samples from which organic matter has been removed using 30 percent hydrogen peroxide (H_2O_2).

1. Record the weight of the wet sediment. Do not allow sediment to dry. Drying can irreversibly alter some sediment characteristics. Moisture content should be determined on separate but representative aliquots of sediment (e.g. channel samples from quartered core sections).

2. The sediments to be analyzed should be prerinsed with the contact liquid; i.e., liquid which is representative of the bottom water of the natural environment in question but without tracer. For example, in normal nearshore marine sediments the contact liquid should be coastal seawater. However, certain offshore areas may be permeated by brackish waters (Hathaway and others 1979); hence, preliminary analysis of the salinity of pore fluids is recommended. Wash the sediment four times with the contact liquid with at least 7-fold the weight of the sediment. Stir the sediment and liquid several times for 15 min each for the first three washes. Allow the sediment to settle, centrifuge for 5 min at 1,000 g or greater, and decant the liquid. Clays may require

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greater forces or longer time. Allow the fourth wash to remain in contact with the sediment for at least 24 h with occasional stirring. Centrifuge and decant the liquid as before. Save the fourth wash solution as an "equilibrated contact solution."

3. Prepare a stock radioactive tracer solution by first evaporating the "as received" radioactive tracer solution. Wet the residue with 6M HCl and allow the solution to evaporate again. Add the contact solution (filtered seawater should be used for marine samples) to dissolve the tracer and allow this solution to stand for 1 week. Filter the solution using a 0.45 micron polycarbonate membrane filter.

4. Determine pH in a sample of the contact solution plus tracer.

5. Place 5 to 25 g of wet sediment into a centrifuge tube or bottle. Add the tracer-spiked contact solution and mix thoroughly. The volume of the solution should be seven times the weight of the sediment. It is strongly recommended that the procedure include evaluation of the adsorption isotherm by making several runs with different concentrations and ratios of solution to sediment. Experiments have shown that R_d will vary with the solution/sediment ratio (Traves 1978, Pietrzak and Dayal 1981). Analysis of R_d at several tracer concentrations is recommended.

6. Run each sample set in triplicate. Shake the contents of each tube on a laboratory shaker for at least 6 h at 3 day intervals. To demonstrate that a steady state has been achieved, you shall have contact periods of 3 to 14 days. Constancy will be observed during the 2nd to 5th shaking-observation cycles. If no steady state is achieved in this time a longer period may be employed.

7. Prepare blank samples by adding aliquots of the stock tracer solution to the contact solution in quantities identical to those used for the R_d determinations. The blanks should stand in similar bottles as the the sediments for the same period of time, and should be filtered in the same manner as the samples. The blanks are used to determine the original activity in the tracer-spiked contact solutions as well as the plateout on apparatus. Blanks should be prepared in triplicate.

8. Measure and report the pH of the mixtures.

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9. Centrifuge each sample for 20 min at a minimum of 1,400 g in a controlled temperature centrifuge. Separate the liquid and solid phases.

10. If filtration is necessary or desirable, use a 0.45 micron polycarbonate membrane filter. Check for presence of species of interest in the filters by the appropriate analytical method (e.g. after ashing in a platinum foil-lined, porcelain crucible). Check for the possibility of tracer adsorption by filtering the original tracer-spiked pre-equilibrated solution and analyzing the filtrate.

11. For each shaking/observation cycle, take an aliquot from the supernate and determine the concentration of the species of interest by the appropriate analytical method.

The formula for calculating the distribution ratio, R_d, for radioactive species is given by:

$$R_d = \frac{A_s \times V_l}{W_s \times A_l}$$

where

A_s = activity of the sediment phase (found by subtracting A_l from the activity of the blank),

W_s = weight of the sediment phase corrected for moisture,

A_l = activity of the solution equilibrated with the sediment, and

V_l = volume of the solution equilibrated with the sediment.

Discussion

This test method applies to porous media in which adsorption and ion exchange are the principal applicable processes affecting radioactive ion distribution between solid and liquid phases. Other processes affecting ion behavior are complex formation (especially with organic matter), precipitation, and co-precipitation. Biomethylation of specific phases (e.g., I, Sb) may solubilize components (Craig 1980).

Although the test is not intended for redox-active species, reactions related to changes in organic-rich, reducing sediments may indirectly affect uptake or release of specific radionuclides through change in physicochemical conditions, sorption, complexation and decomplexation. Special precautions may be required for given tracer solutions. For example, evaporation of stock tracers to dryness may volatilize iodine, and render plutonium insoluble.

The effective diffusion coefficient, governed by the tortuosity of the fluid pathway through the sediment, can be estimated for nonreactive ions by resistivity methods (Manheim and Waterman 1974, Andrews and Bennett 1981), or by the tracer-implant method (see Sayles 1984). An important additional factor affecting ion transport in sediments is bioturbation. For a treatment of this phenomenon and chemical models describing it, see Aller (1982).

Measurements of pH are useful to characterize conditions under which the laboratory measurements are carried out, but pH values on sediments recovered from marine environments are usually unreliable because of outgassing during sediment recovery. In situ pH values can be better computed from interstitial water measurements (Manheim and Schug 1978).

Quality Assurance

The estimated overall precision of measurement is 10 to 25 percent in terms of a coefficient of variation for R_d values in the range of 1 to 400 mL/g. Error analysis may be treated by standard statistical methods (ASTM 1976). More direct control on ion transport measurements in sediments is through in situ implanted tracer experiments (Sayles 1984). These and appropriate porefluid studies also offer a means of evaluation of labile or redox-active radionuclide transport in recent marine and nonmarine sediments.

Cost Analysis

Time required for batch R_d determination   16 hours

    COST PER ANALYSIS AT BATCH RATE $ 1,000

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CHAPTER 7

IRON AND MANGANESE

Introduction

The following procedures for determining the concentrations of Fe and Mn in marine sediments are taken from a general analytical scheme which is appropriate for subsequent analysis of other metals. The procedures presented were developed for analysis of Al, Ba, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, V, and Zn in marine sediments from the continental margin off the eastern United States (Bothner and others 1984).

The methodology is appropriate for sediments having a wide range of grain size. With a carbonate-rich sample, slowly add the acid to avoid sample loss with the effervescence caused by the generation of CO_2. The low drying temperature used in our procedures minimizes the loss of volatile forms of mercury that may be present.

Profiles of Fe and Mn can be used to locate the boundary between oxidizing and reducing conditions. Chapters 8 and 9 also present methods for locating this boundary.

Procedure

An aliquot from a well-homogenized original sample is dried at 70 °C for 24-48 h until constant weight is achieved. The dried sample is ground in an agate grinder to avoid the contamination introduced by some other grinding materials (cobalt, for example, from tungsten carbide grinders).

Two blanks containing all reagents are analyzed along with the samples. All reagents are analyzed for contaminants prior to use, as is always necessary. The Canadian marine sediment standard MESS-1 (Marine Analytical Chemistry Standards Program, National Research Council, Canada) and the US Geological Survey marine sediment standard MAG-1 (Flanagan 1976) are analyzed in each set of samples. A series of solution standards is prepared which approximates the concentration levels expected in the samples; this series is used as the standard in calibrating the inductively coupled plasma (ICP) spectrometer.

Exactly 0.5 g of ground bulk marine sediment is added to a covered teflon beaker and digested overnight (at least 8 h) with 5 ml of 72 percent $HClO_4$, 5 ml of HNO_3, and 143 ml of HF at approximately 140 °C. The next day, the covers are removed and the temperature is increased to between 180 and 190 °C, first producing fumes of $HClO_4$ and then evaporating the solution to dryness. Care should be taken that easily oxidizable organic matter is already consumed before the drying step. The residue is

dissolved and diluted to exactly 25 ml with 8 N HCl. This solution is referred to as stock solution A.

The concentration of Fe and Mn is determined by inductively coupled plasma (ICP) spectrometry by using 1 ml of stock solution A diluted to 10 ml with distilled H_2O. The instrument used is a Jarrel Ash Plasma Direct Reader, model 1160. The argon plasma torch is maintained by an induction field having a frequency of 27.1 MHz. Aerosols aspirated into the plasma are ionized and the characteristic radiation of the elements are measured spectrophotometrically. Instrument conditions: argon gas, 20 l/min; wavelength for Fe, 259.9 nm; wavelength for Mn, 257.6 nm; forward power, 1.1 kw; fixed cross flow nebulizer; spectral band width, 0.036 nm; observation height, 16 mm; sample flow rate, 0.8 ml/min.

For Fe, the determination limit for this procedure is 50 ug/g in the bulk sample. The average blank, as measured in solution, is 0.02 ug/g.

The determination limit for Mn is 10 ug/g in the bulk sample. The average blank, as measured in solution, is 0.006 ug/g.

Atomic absorption spectrophotometry is an alternative method for the analysis of digested marine sediment (Buckley and Cranston 1971).

Quality Assurance

Procedures for quality assurance typically include replicate analyses of sediment standards and comparison of results with certified values. The precision of Fe and Mn analyses, as determined by the coefficient of variation for 12 replicates of standard sediments, is approximately within 4 percent. The accuracy of the methods is determined by comparing absolute values determined with published "accepted values." For 12 replicates of the standard MESS-1, measured Fe was equal to 2.92 +/- 0.04 percent. The published value is 3.0 +/- 0.2 percent[1]. Mn was measured at 476 +/- 18 ppm; the published value is 513 +/- 25 ppm[1]. For five replicates of the USGS marine sediment standard MAG-1, Fe was measured at 4.7 +/- 0.1 percent and Mn at 721 +/- 11 ppm. "Best" accepted values are 4.9 percent for Fe and 710 ppm for Mn (Bothner and others 1984).

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[1]   Values reported by the Marine Analytical Chemistry Standards Program, National Research Council, Canada.

Cost Analysis

The following estimated cost analysis of Fe and Mn presumes an adequately equipped laboratory and large (greater than 40) batches:

COST PER SAMPLE AT BATCH RATE $ 50[*]

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[*] Additional elements can be analyzed by ICP without further separation at $ 7 per element.

Atomic absorption spectrophotometry (AAS) is another method commonly used to determine the concentrations of metals in digested sediment samples. The advantage of the ICP instrumentation is that a number of elements can be determined in the sample solutions simultaneously and, in some cases, with greater precision at low element concentrations. If both types of instrumentation are available, the use of ICP for determination of Fe and Mn is more cost effective than the use of AAS.

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CHAPTER 8

NITRATE

Introduction

The objective of this method is to present techniques for determining interstitial nitrate profiles in marine sediments. This parameter permits assessment of the degree of oxidation in marine sediments in proposed or existing low-level nuclear waste disposal sites. The rationale is that the depth where interstitial nitrate concentrations approach zero marks the level below which redox-active radionuclides undergo major changes in solubility. Some elements like Fe, Mn, Ce and Co may become more mobile, whereas others like U, Pb and Cu may become less mobile as a consequence of forming sulfides or other less soluble compounds. Because nitrate is a highly labile component, careful attention to sampling (see Chapter 2) and pore fluid extraction technique is required. Two in situ techniques that require no separate sediment sampling are in current use: (1) in situ probes (Sayles and others 1976), and (2) "peeper" techniques that allow ions to migrate from the sediment across membranes into the sampler (Kepkay and others 1981). However, the methods and equipment are expensive, not commercially available, and do not easily provide detailed interstitial gradients at intervals less than a centimeter. Therefore, these approaches are not recommended unless the laboratory doing the monitoring is already familiar with them. The method proposed here involves fluid extraction from a core sample and nitrate analysis. These two steps will be treated in the remainder of this chapter.

Porewater Extraction

Once an acceptable core is at hand, there are two ways to extract porewaters from slices of sediment: centrifugation and squeezing. Ordinary contact between porewaters and the apparatus used for these two techniques does not appear to alter interstitial nitrate concentrations. There is, however, a general source of contamination that must be avoided. Exposure of reducing sediment to air can cause significant increases in interstitial nitrate levels (Fanning and Maynard-Hensley 1980). It can even make nitrate appear when none was present. This limitation affects the choice of extraction apparatus and the length of storage of samples, which should not be for more than a few hours (for a more complete discussion of handling and storage, see Chapter 2). Porewater extraction by centrifugation is simple. Sediment is extruded and sealed in centrifuge tubes to await centrifugation. Typical centrifuging conditions are 15,000 rpm for 3-4 min (Froelich and others 1983). Thus 15 to 20 sediment samples can be processed per hour. Fifty cm^3 of sediment can be put in each tube so reasonably large porewater samples are obtained. Extruded pore waters will have some

turbidity and should be membrane-filtered. This is done by expelling pore fluid from a Luerlok syringe (disposable plastic syringe whose tip locks onto a filter device) through a Swinney filter attachment containing 1-cm diameter 0.4-u Nuclepore membranes. The principal disadvantage of centrifugation is that a suitable centrifuge such as a Sorvall SS3 is difficult to use at sea; gimbaled platforms are necessary. The alternative is to store the sediment in centrifuge tubes and spin them back on land. However, sediment should not be stored in this fashion more than a few hours, and logistics will rarely accomodate this requirement. Transfer of core sections to containers flushed with inert gas may be possible but still poses the risk that hard-won samples may yield uncertain data. Therefore, for most monitoring operations, sediment squeezing is the recommended method of porewater extraction, even though squeezers appropriate to process large numbers of samples are difficult to obtain commercially.

The recommended squeezer is plastic (Nylon or Delrin) with a gas-driven membrane that presses whole sediment against a filter to express porewater. For most unconsolidated marine sediment, a high-pressure stainless-steel squeezer (Manheim and Gieskes 1984) is not needed. There are two principal types of plastic membrane squeezers. One is the Reeburgh (1967) squeezer which is held together by a metal C-clamp. The second is the threaded type (Fig. 11) in which the top screws into the bottom. Although threaded squeezers are more complicatad in construction, they have operational advantages over Raeburgh squeazers. Metal clamps corrode, and Reeburgh squeezers are difficult to clean. The threaded types, suited for multi-unit deployment on a gas manifold, are depicted in Figure 11, and are the basis of this method. The plastic top is screwed in and out of the base with a question mark-shaped wrench. The stem of the question mark is the handle, and a small rod protrudes from the internal curved portion near the top. That rod fits into horizontal holes drilled into the squeezer top. Ten threaded squeezers may be operated at once inside a glove bag. Each has a Swagelok quick-connect fitting in its top to deliver squeezing gas (N in Fig. 11) and a Clippard 3-way pneumatic valve to allow it to be operated independently of the rest. Cost for building a threaded squeezer, including tubing and fittings, is modest. The diameter of the filter in Figure 11 is 9 cm, equalling standard laboratory filter paper size. To be absolutely certain that this source of error does not occur, one should process all sediment inside a glove box or bag containing an inert atmosphere (N_2, Ar, or He). However, such an approach is tedious and slow, and an alternative is to let sediment color be the guide (Fanning and Maynard-Hensley 1980, Lyle 1983). If all of a sediment core inside the liner appears to be brown or tan, there will probably be a negligible air artifact, and the sediment can be sliced and centrifuged or squeezed in air. If the core seems to have zones which are green, gray, or black, then
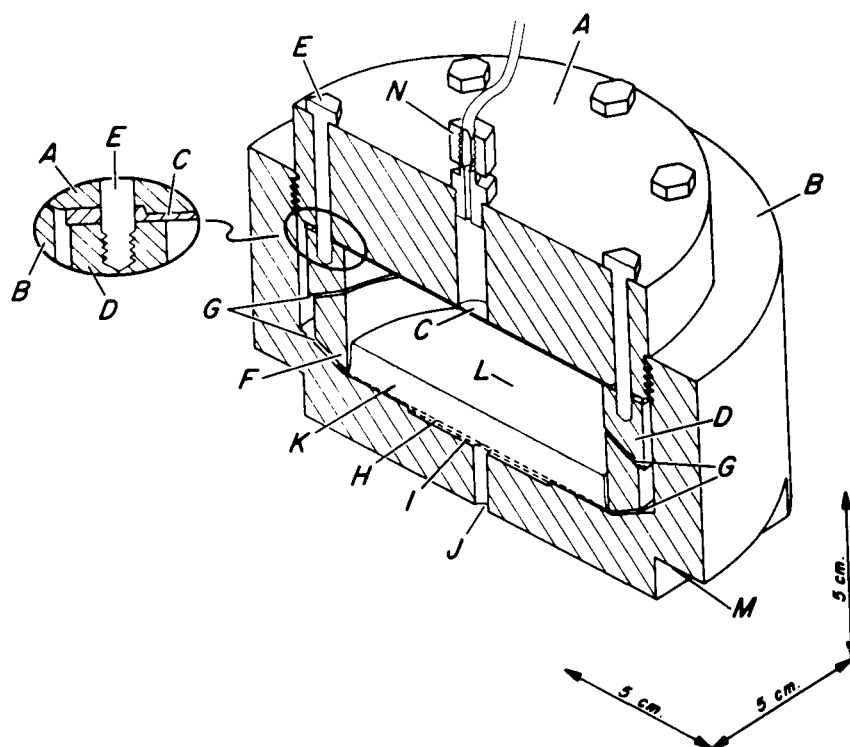
Figure 11. Gas-displacement squeezer for use with multisqueezer mani-
fold. A = threaded squeezer top; B = squeezer bottom with
inner taper (G); C = rubber membrane; D = sealing ring with
tapered edge (G); E = nylon screw; F = inner ring with two
tapered edges (G); G = sealing tapers; H = paper filter;
I = Nucleopore membrane; J = exit hole; K = sediment
sample; L = plastic covering on sediment; M = locking notch
for tightening top.

the sediment is probably reducing and a glove bag or box is necessary. Note that sediment tends to streak along the liner wall during penetration, which may mask the color of the bulk of the sediment at a given level. If sediment from an area is being sampled extensively, tests can be run on some initial cores to determine whether or not an inert atmosphere is required.

Many varieties of glove boxes or bags are available, ranging in price from tens (disposable plastic) to thousands of dollars. All of them present common problems as may be noted in Figure 12. First, the core liner or subcore tube (A) must be transferred into the bag or box in such a way that air is kept out. An effective seal is flexible rubber sheeting (B) held by a Plastic ring (C). The next problem is sediment extrusion. After the core liner is sealed and an inert atmosphere established around it, the core cap may be removed and the supernatant water sucked off. Then the bottom core cap may be removed, and a rubber stopper (D) inserted to serve as a piston. The stopper and sediment remain in place because of the rod (E) and floor mounting (F), while the operator's surgically-gloved hands through the ports (G) move the liner downward to extrude sediment for slicing. The coupling (H) is necessary to allow changing to different lengths of rods as the length of unprocessed sediment shortens during the slicing. A third problem is determining when atmospheric oxygen has been reduced to a safe level inside the bag or box. Some bags require positive internal pressure to avoid collapse. The inflation process (with inert gas) will lower the oxygen concentration considerably, and opening a small exhaust port and continuing to sweep the gases out of the bag for 20-30 min before opening the core will lower it even further. A convenient test is to check whether or not a cigarette lighter can be made to light. This test should be performed periodically as a core is processed. A fourth problem is getting a rack of squeezers (I) inside a glove bag or box. A rack that contains 10 squeezers such as those shown in Figure 12 is at least 2 ft high and at least 3 ft wide. Many glove bags do not have entry ports large enough to accommodate such a structure, and many glove boxes are not tall enough.

      1. Exit port. The exit port (J, Fig. 11) is designed to admit the tip of a Luerlok syringe. Holes are drilled in caps from 1-oz Nalgene polyethylene bottles. Hole size matches the tips of disposable syringes. Disposable syringes are cut off at the upper part of the barrel and inserted into the exit port of each squeezer so that the cap of the 1 oz bottles is held against the bottom of the squeezer. Polyethylene bottles to receive the expressed pore water can then be screwed to the caps beneath the squeezers.
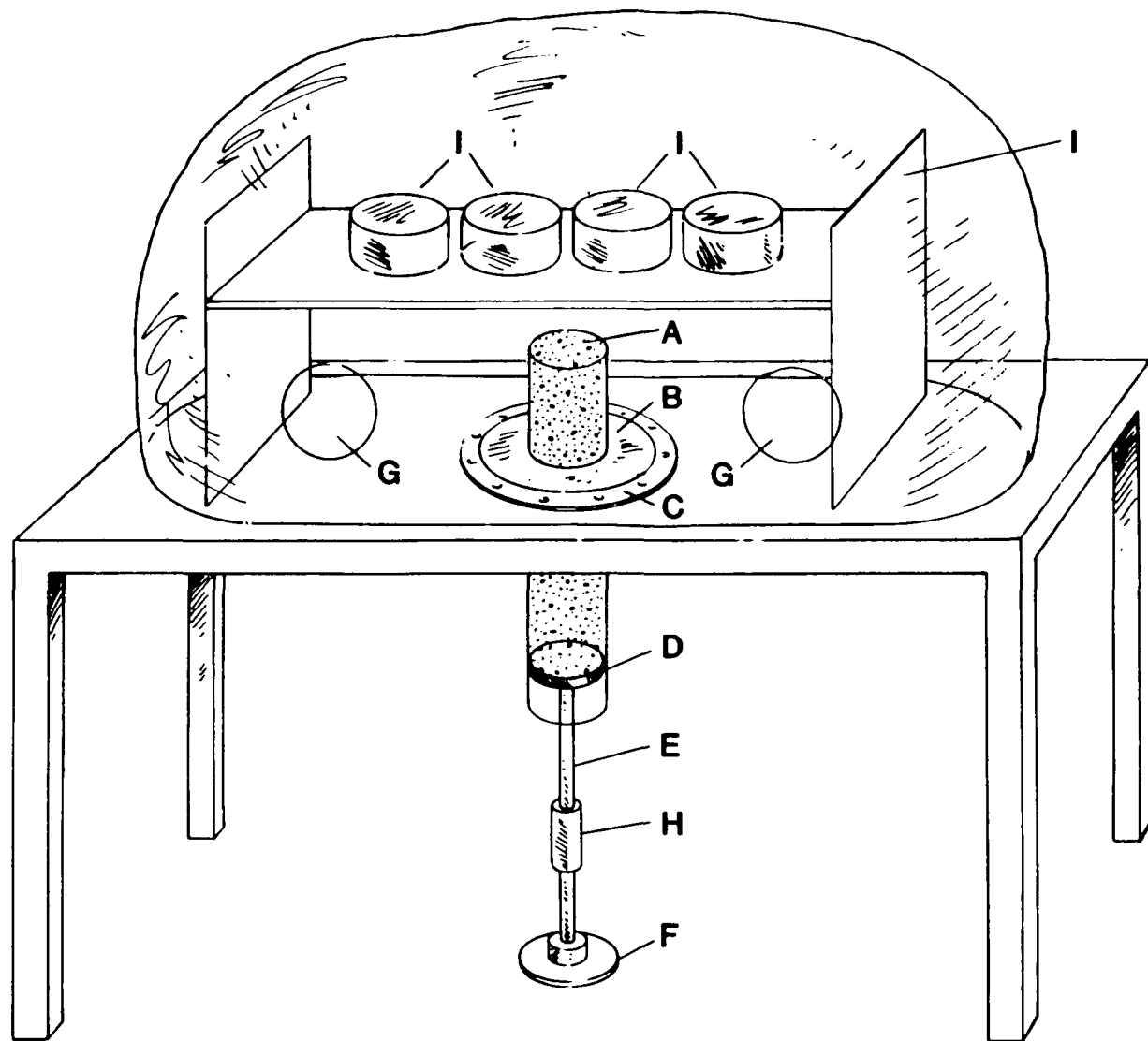
Figure 12. Schematic diagram of an inert-atmosphere system for extruding, slicing, and squeezing sediment. Labeled components are discussed in the text.

2. Installation of the filters. Final filtering of
expressed porewaters is automatic because the central
well in the squeezer is machined to fit a 47 mm 0.4-u
Nuclepore membrane (I). In the well is placed a Whatman
42 (or equivalant) paper filter (H) which is wide enough
to fit between the lower tapered surface (G) of the inner
ring (F) and the tapered portion (G) of the squeezer
bottom. This arrangement makes a good seal to keep the
sediment from being extruded between the inner ring and
the squeezer bottom while the porewaters pass through the
two filters. (A problem with a Reeburgh squeezer is that
sediment extrusion into the 0-ring channel on the bottom
edge of the cylinder makes it hard to clean).

3. Loading of sample into the squeezer. First, a
sediment slice is extruded from the liner and the outer
contaminated layers scraped off. The sediment (K) is
placed on the filter paper and covered by a circle of
thin polyethylene film (L) wide enough to fit between the
inner ring (F) and the squeezer bottom. The sediment
thus becomes the "meat" in a "sandwich" of filter paper
on the bottom and polyethylene sheeting on the top.
Sediment flow outside the "sandwich" is minimal. The
compacted sample is easy to remove and put in plastic
bags for subsequent chemical or mineralogical analysis.
Cleanup between samples is quick and easy. All that is
necessary is to wipe the squeezer parts with a Kimwipe
tissue. It is almost never necessary to clean the rubber
membrane in the top. Much time is thereby saved when
processing large numbers of sediment samples to define
interstitial gradients. Sediment should always be spread
out in as thin a layer as possible, no more than 1 cm.
When thicker layers are squeezed, the sediment next to
the filter compacts during the first part of the
squeezing process and inhibits percolation from porewater
farther from the filter, reducing yield.

4. Completing the squeezing. The top of the squeezer is
screwed on and tightened with a wrench (note in Figure 11
that the bottom has notches to hold it during the
tightening). Inert gas is admitted slowly to expand the
membrane (C) against the polyethylene film (L). Most of
the porewater should flow into the receiving bottle in a
rush after a pressure increase of less than 5 psi. The
pressure is increased to 120 to 160 psi and held for 5 to
15 min. The receiving bottle with the porewater sample
is removed and capped, after which the squeezer is
disassembled, cleaned and reloaded for the next sample.
The Nuclepore membranes can even be dried with tissue and

re-used; polycarbonate is tough. A normal porewater yield is 10 to 15 cm^3 from a 40 cm^3 sediment sample, which is about 50 percent of the porewater present in the sample. Although optimum results are assured by on-board analysis of samples within a few hours of extraction, pore fluids may be frozen in well-sealed containers flushed with inert gas, and analysis deferred for several days.

Nitrate Analysis

Nitrate dissolved in pore waters cannot be easily measured. Therefore it is reduced to nitrite in a Cd-Cu reductor, and the nitrite is measurad colorimetrically. The reaction between NO_2^- and sulfanilimide produces the diazonium ion which is then reacted with N-(1-naphthyl)-ethylenediamine dihydrochloride to form an intensely rose-colored azo-dye. That color is measured at 520 to 540 nm in a spectrophotometer or colorimeter. The procedure was first described for seawater by Bendschneider and Robinson (1952). Porewater may contain nitrite as well as nitrate. Therefore the effluent from the Cd-Cu reductor may contain more nitrite than that produced from nitrate. To obtain interstitial nitrate levels, you must conduct two analyses on each porewater sample. One analysis determines the concentration of nitrite alone, and the other determines the concentration of nitrite + nitrate in the reductor effluent. The nitrate concentration in the porewater sample is then estimated by difference.

Porewater is usually obtained in small volumes. A 10 to 15 cm^3 of porewater is a large sample. This presents a problem because the well-established manual methods for nitrate determination are set up for 50 to 100 cm^3 samples (Strickland and Parsons 1972, Grasshoff 1976). A scaled-down manual method is not available and, even if it were, would probably result in large errors. Porewater samples could be diluted; however the sedimentary regions of greatest interest are those with low porewater nitrate profiles. Dilution of the porewater nitrate concentrations would be counterproductive to a precise definition of the profiles in those regions. The desired analytical method will utilize from 1 to 3 cm^3. Automated analysis such as performed on an autoanalyzer can meet this need. Typical sampling times are 0.5 min which, according to the flow charts for the nitrite and nitrate + nitrite methods in Figures 13 and 14, will consume only 0.37 cm^3. The proper procedure is to place 0.5 cm^3 of porewater in a 4-cm^3 autoanalyzer sample cup for a nitrate analysis.   A duplicate determination thus consumes only about 1 cm^3, or 10-15 percent of a typical porewater sample. This provides an inducement for using an autoanalyzer method, which is faster than a manual method and more reproducible because

TECHNICON AUTOANALYZER METHOD NITRITE
CONCENTRATION RANGE 0-3.00μM
TYPE SAMPLE SURFACE, SALINE AND PORE WATER
REFERENCE AA II

RATE: 30 PER HOUR
(2:1)

SAMPLER IV

	TUBE SIZE (inches)	COLOR CODE	FLOW RATE (ml/min)
TO SAMPLER ← SAMPLE / WASH	.073	GREEN-GREEN	2.00
AIR	.030	BLACK-BLACK	0.32
COLOR REAGENT	.035	ORANGE-ORANGE	0.42
SAMPLE	.035	ORANGE-ORANGE	0.42
← WASTE	.035	ORANGE-ORANGE	0.42

20-TURN COIL   20-TURN COIL

F/C PULL THRU

PROPORTIONING PUMP

COLORIMETER   RECORDER
50 mm TUBULAR F/C
520 mμ FILTERS
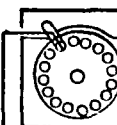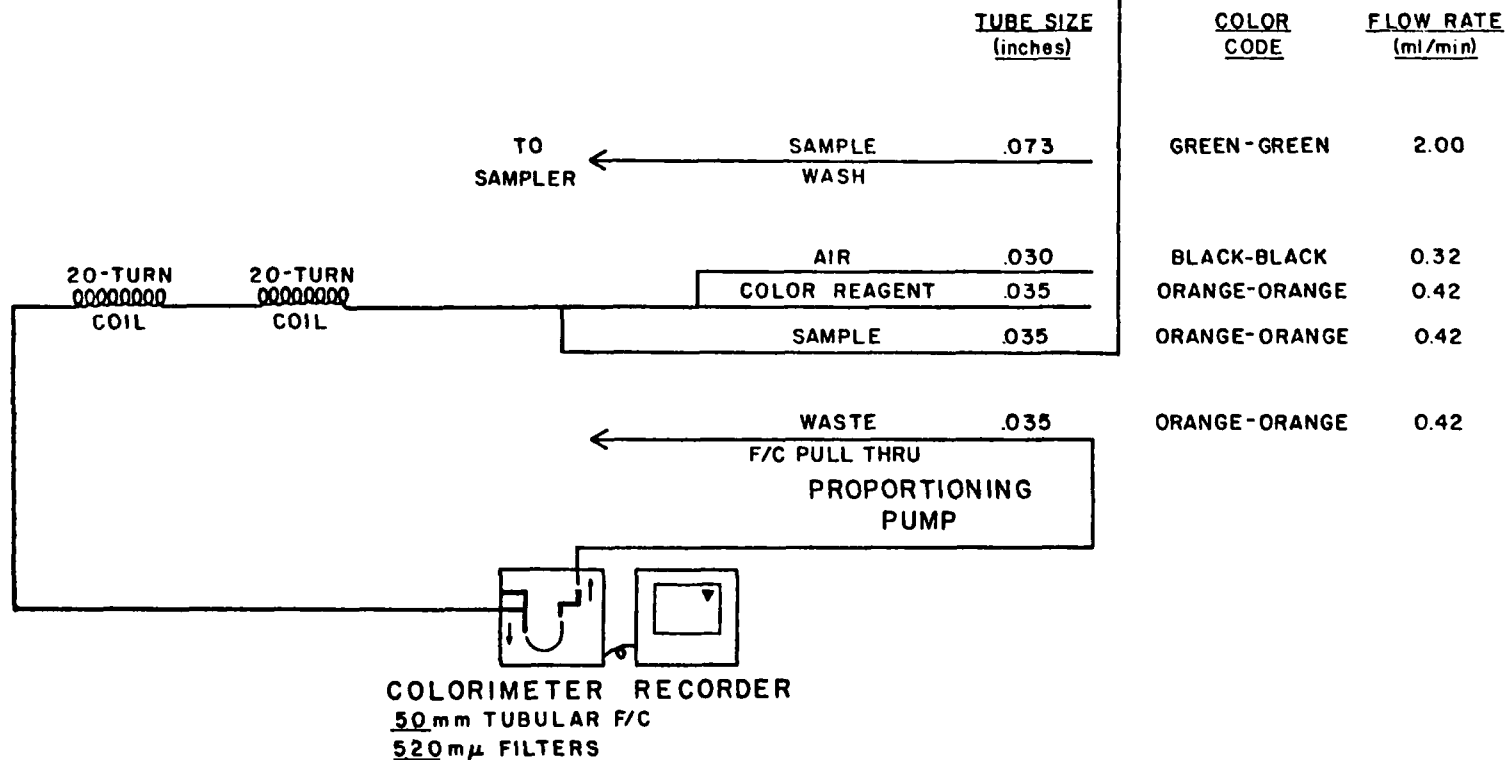
Figure 13. Schematic diagram of the configuration of a Technicon Auto-analyzer II for the determination of dissolved nitrite. The color codes listed are for the various sizes of tubing used in the configuration.

TECHNICON AUTOANALYZER METHOD NITRATE + NITRITE
CONCENTRATION RANGE 0-50μM
TYPE SAMPLE SURFACE, SALINE AND PORE WATER
REFERENCE AAII

RATE: 30 PER HOUR
(2·1)
SAMPLER IV

WASTE
RESAMPLE LINE
POLYETHYLENE
TUBING

REDUCTOR
COLUMN

5-TURN
COIL

20-TURN
COIL

PROPORTIONING
PUMP

COLORIMETER RECORDER
50 mm TUBULAR F/C
520 mμ FILTERS

	TUBE SIZE (inches)	COLOR CODE	FLOW RATE (ml/min)
AIR	.030	BLACK-BLACK	0.32
AMMONIUM	.056	YELLOW-YELLOW	1.20
CHLORIDE			
SAMPLE	.030	BLACK-BLACK	0.32
AIR	.030	BLACK-BLACK	0.32
COLOR	.030	BLACK-BLACK	0.32
REAGENT			
SAMPLE	.073	GREEN-GREEN	2.00
WASH			
F/C WASTE PULL THRU	.051	GRAY-GRAY	1.00
COLUMN WASTE	.040	WHITE-WHITE	0.60
PULL THROUGH			

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Figure 14. Schematic diagram of the configuration of a Technicon Auto-
analyzer II for the determination of dissolved nitrate +
nitrite. The color codes listed are for the various sizes
of tubing used in the configuration.

both samples and standards are processed under carefully controlled timing and operational conditions. Autoanalyzers are common to many water quality laboratories, and, although the initial cost of the instrument is high, operating expenses are reasonable.

The procedure for a specific system, the Technicon Autoanalyzer II, is as follows:

Samples are placed in the 4-cm^3 plastic sampling cups which are arranged in a circle around a tray. The mechanical sampler inserts a stainless steel tube in each cup and sucks out sample for a carefully controlled time period. The tube is withdrawn, placed in a deionized water wash for another carefully controlled time period, and then inserted in the next sample cup along the tray. During the wash step, deionized water is sucked into the system such that samples, standards, and blanks are separated from each other by pulses of wash water. Air bubbles are inserted at regular intervals along the stream of samples, standards, blanks, and wash water to prevent those entities from blending with each other due to backward streaming of liquids along the tubing walls. Color is developed downstream of the sampler after reagents are added to the stream and the mixture passes through mixing coils (Figs. 13 and 14). A peristaltic pump both sucks and moves samples and injects reagents. The air bubbles are removed just before the stream in which color is developing passes through a flow cell in a colorimeter. There the intensity of the color is sensed and appears as a series of peaks on a moving strip chart. The heights of the peaks are measures of the concentrations of the substance of interest in the various samples, standards, and blanks being analyzed. Further details may be found in the standard references of Strickland and Parsons (1972), Grasshoff (1976) and in the Technicon literature (Technicon Industrial Methods 161-71W/B, 1976, and 158-71W, 1972). Since nitrite and nitrate + nitrite will be analyzed on the same porewater sample, time can be saved by sampling for both methods from the same 4-cm^3 cup and using a splitter to divide the stream out of the stainless steel sampling tube. Tubing on the output nipples of the splitter can be selected to provide the input flow rates recommended for each method: 0.42 ml/min for nitrite (Fig. 13) and 0.32 ml/min for nitrate + nitrate (Fig. 14).

Nitrite

Refer to Figure 13 during this discussion. Only one reagent is required, the DIAZO color reagent which is labelled COLOR REAGENT in Figure 13. It is prepared as follows:

Sulfanilamide ($C_6H_8N_2O_2S$)	5.0	g
Concentrated Sulfuric acid	50.0	ml
N-(1-naphthyl)-ethylenediamine dihydrochloride		
($C_{12}H_{14}N_2O_2 2HCl$)	0.25	g
Brij-35	0.5	ml
Deionized water	500.0	ml

Add 50 ml of concentrated sulfuric acid and 5.0 g of sulfanilamide to 350 ml of deionized water. Some heating may be necessary to dissolve the sulfanilamide although the heat of dilution of the concentrated acid is usually sufficient. Dissolve 0.25 g of N-(1-naphthyl)-ethylenediamine dihydrochloride and 0.5 ml of Brij-35 in the solution. Dilute to 500 mL with deionized water.

The DIAZO color reagent should be kept in a dark bottle and stored in a refrigerator (4 $^{\circ}C$); it should last 2 to 3 months if so preserved. Brij-35, a reagent supplied by Technicon, controls air-bubble surface tension and wall friction inside the tubing carrying the sample stream. The control is necessary to guarantee that the air bubbles are of uniform size and spacing. Brij-35 is very important; without it or with too little of it, peaks on the strip chart become erratic and very difficult to read. If the DIAZO reagent has a pinkish caste after preparation, discard it and try again with fresh reagents. The old reagents are probably contaminated.

Two types of standards are required. The first is the Stock standard which is very concentrated and is used for a long time. The second is the Daily standard which is prepared by diluting the Stock standard every time samples are run. Preparation protocol is as follows: Stock standard -- 5 mM NO_2^-. Dry reagent grade $NaNO_2$ and weigh out 0.3450 g to +/- 0.1 mg. Dissolve in a little deionized water in a 1-liter Class A volumetric flask. Add a few drops of chloroform ($CHCl_3$) and dilute to the mark. Daily (or working) standards -- prepare four or five working standards by diluting aliquots of the Stock standard with seawater. Use Class A volumetric flasks. The range of the working standards should be 0 - 5 uM.

Chloroform is added to the Stock standard to retard bacterial activity, and, if the Stock standard is kept in a dark bottle, it can last for up to a year. The Daily standards are

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made up in seawater because of refractive index changes that occur
in the colorimeter flow cell when the boundary between a porewater
sample and the deionized water wash solution crosses the light
path. If the working standards are made up in seawater, then the
refractive index changes are the same for both samples and
standards. Almost any seawater will do, as long as it is not
anoxic and has a salinity of at least 33. Open-ocean surface
seawater is preferable, if available.

A blank solution is required because almost no seawater
can be guaranteed to be "nitrite-free." A 0.7-M NaCl solution is
an excellent blank solution. There is a possibility that some
reagent-grade NaCl is slightly contaminated with nitrite.
Therefore, the analyst should first prepare two blank solutions:
one made with ULTREX NaCl and the other with ordinary
reagent-grade NaCl. If the reagent grade gives a peak with a
height greater than that of the ULTREX NaCl, then the
reagent-grade NaCl should be re-crystallized once or twice to
remove the nitrite contamination.

The following protocol should be followed in performing
nitrite analyses on porewaters. Configure the Autoanalyzer
according to Figure 13. Run all samples in duplicate, and run a
set of standards and blanks for every 20 samples. Adjust the
baseline to between zero and 3 percent. Adjust the gain until the
peak for the most concentrated working nitrite standard is nearly
full scale on the recorder (90 - 100 percent). The cam in the
sampler should be selected so that the sampling tube is in each
cup for 0.5 min. Wash time should be selected to give suitable
separation between sample peaks. Then the run of samples,
standards, and blanks should be completed. Measure the heights of
the peaks (PH) above the baseline on the strip chart (a low-level
nitrite peak often resembles two mountains connected by an
elevated plain). The peak height is the distance from the
baseline to the elevated plain. Nitrite concentrations should be
calculated according to the following equation:

$$[NO_2^-] = (PH_{sample} - PH_{blank}) \times F$$

"F" is the least-squares slope of the regression of
concentration vs. peak height for the set of working standards for
the run. A sample of the diluting seawater for those standards
should be given a "zero" concentration, and the concentrations of
the other standards calculated on the basis of that assumption and
the nitrite added in the aliquots of the Stock standard. Use of
the 0.7-M NaCl blank solution corrects for the fact that the
diluting seawater may contain some nitrite.

Nitrate + Nitrite

The protocol for the Autoanalyzer processing of nitrate +
nitrite has two main parts (Fig. 14). In the first, the sample

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stream comes from the sampler (or one outlet of the sample splitter), is injected with air bubbles and ammonium chloride solution, is de-bubbled, and flows into the Cu-Cd reductor column where the nitrate is reduced to nitrite. Then, in the second part, the effluent from the reductor column is re-injected with air bubbles, is injected with color reagent which reacts with the nitrite, and is de-bubbled and passed through the colorimeter flow cell as in the nitrite method.

The first preparation the analyst must make is the Cu-Cd reductor column (Fig. 15). Two solutions are required to make and maintain the reductor columns: (1) a solution of 10 g NH_4Cl per liter to which 3-5 drops of concentrated NH_4OH has been added to achieve a pH of 8.5 and, (2) a 2 percent W/V solution of $CuSO_45H_2O$. Suitable Cd filings or powder (40-60 mesh) may be purchased from chemical supply companies. Also needed are Cu filings or powder in 20-40 mesh. Prepare a mixture of the two which is about 5 percent, i.e., 1 Cu grain for every 20 Cd grains. Wash the mixture with diethyl ether and 1N HCl, rinse with deionized water, and allow to dry. Wash about 8 g of the dried mixture with the $CuSO_4$ solution and rinse thoroughly until the colloidal Cu is removed -- about 10 times. The Cd grains should be black. The reductor column is 2 mm I.D. and 100 mm long; they can be made or purchased as empty u-shaped tubing from Technicon (Fig. 15). The empty reductor column is filled with deionized water and the mixture of Cu and Cd grains is transferred using rubber tubing, a small funnel, and forceps. Care must be taken to avoid trapping air bubbles between the grains. Plug the column ends with glass wool.

The color reagent in Figure 14 that is mixed with the effluent from the Cu-Cd reductor column is the same DIAZO color reagent as in the nitrite method discussed previously. All the same techniques and precautions apply.

A Stock standard and Daily (working) standards are used in the nitrate + nitrite method. The preparations are as follows:

Stock standard -- 5 mM NO_3^-

Dry reagent grade KNO_3 and weigh out 0.5056 g to the nearest 0.1 mg. Dissolve in a little deionized water in a 1-liter Class A volumetric flask. Add 1 ml of chloroform ($CHCl_3$) and dilute to the mark.

Daily (or working) standards

Prepare four or five working standards by diluting aliquots of the Stock standard with seawater. Use Class A volumetric flasks. The range of the working standards should be 0 to 40 uM for most porewaters although it could be less for more reducing sediments.

N6
NIPPLE

GLASS
WOOL

1/8" × 1/4"
SLEEVE
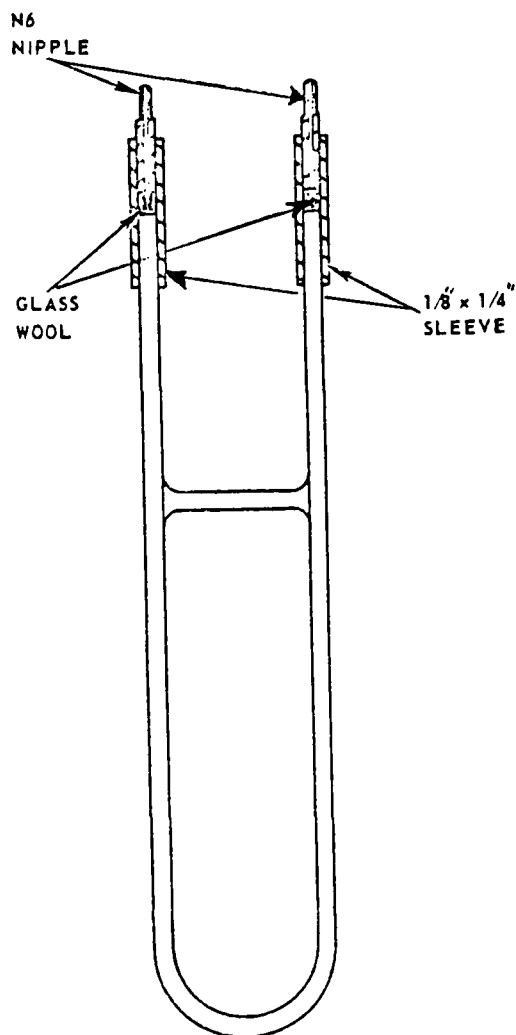
Figure 15. Cadmium-copper reductor column for the
determination of nitrate + nitrite in
marine porewaters. The column shown is
of Technicon design with fittings that
attach to a Technicon Autoanalyzer II.

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If kept in a tightly capped dark bottle, the Stock standard should last for months since the $CHCl_3$ retards bacterial activity. Working standards are made with seawater to guarantee that refractive index changes are the same for both samples and standards. This approach is similar to that used in the nitrite method. However, in the case of the nitrite + nitrate method, the seawater should be surface seawater reasonably far from land. Deeper seawater or seawater too close to land can have as much nitrate as porewaters. Salinity should be at least 33. A 0.7-M NaCl blank solution is used for the same reason and with the same precautions for the nitrate + nitrite method as for the nitrite method. The Autoanalyzer should be configured according to Figure 14. All samples are run in duplicate, and a set of standards and blanks as run for every 20 samples. An important beginning step is to "activate" the Cu-Cd reductor column by passing a seawater solution rich in nitrate through it. A 2-mM solution is recommended, and 2-3 cups in the sampler tray should be filled with this solution. This "activation" process is necessary to make certain that the first sample or standard to pass through the reductor is reduced with the same efficiency as all the other samples and standards. Without "activation" the reductor may not reach maximal efficiency until several standards or samples have passed through. One should avoid connecting the color reagent line to the reductor effluent until the large nitrate "spike" has passed. Otherwise, an intense purple color forms that has to be washed out before other samples can be processed. The nitrate + nitrite run proceeds similarly to a nitrite run. Sampling time is 0.5 min, wash time is selected to optimize peaks; baseline and gain are adjusted by the same criteria; and peak heights are determined the same way. Concentrations of nitrate + nitrite are calculated by the equation:

$$[NO_3^- + NO_2^-] = (PH_{sample} - PH_{blank}) \times F$$

"F" is the least-squares slope of the regression of concentration vs. peak height for the set of working standards for the run. Because the Stock standard is so high in nitrate, only small aliquots will be necessary to prepare the working standards, and all of them can be considered to have the same low nitrite concentrations. For the purpose of obtaining the factor "F," it is reasonable to assume that nitrite concentration is zero. Therefore, the concentrations used in the standardization regression are taken to be the same as the increases produced by the standard additions of nitrate. As with the nitrite method, use of the 0.7-M NaCl blank solution corrects for the fact that the diluting seawater may contain some nitrite or nitrate. When a run is over the NH_4Cl solution should be pumped through the Cd-Cu reductor column. The lifetime and functioning of the column are greatly enhanced by storage in NH_4Cl. The reductor column has a finite lifetime, and it is critical to test the column periodically for reduction efficiency. The test is to add spikes

of $NaNO_3$ and $NaNO_2$ to the same sample. The additions should be such that both the nitrate and nitrite concentrations in the sample are to be increased 10 M higher. Then the sample is passed through the nitrite and the nitrate + nitrite protocols simultaneously in the normal way. The increases in peak heights, for the altered sample will show whether or not the reducing efficiency of the reductor column is suitably close to 100 percent. Air bubbles are a serious problem in the reductor column. The column should be installed with no bubbles entering at the connectors, and columns separated from the Autoanalyzer should be stored with NH_4Cl-solution-filled Tygon tubing between their ends.

Quality Assurance

Because of the labile nature of nitrate and the fact that relatively few sets of analyses have been performed with this method, determination of the accuracy of the test has not been feasible. Precision has been examined, however. Using the percent recovery test (EPA 1979), in which a controlled nitrate spike is run on the autoanalyzer, an 85 percent recovery was accomplished at a concentration of 2 uM and a value of 98 percent was achieved at a 10-uM concentration. Replicate analyses, in the range from 0 to 30 uM, yielded a maximum standard deviation of 0.3. In addition, 58 pairs of duplicate analyses on stream samples showed an average range of difference of 0.8 uM.

As stated previously, data quality is the most vulnerable when an orignally "reduced" sample is exposed to oxygen. Furthermore, nitrate can be lost from an oxidized sample if the sample is sealed off from oxygen. For this reason, samples should be processed within a few hours of core recovery.

Cost Analysis

COST PER ANALYSIS AT BATCH RATE $ 450

Discussion: Alternative Methods To Measure Oxidation State

The simplest alternative to nitrate measurement as a monitor of oxidation state in sediments is color. The boundary between oxygenated and anoxic sediments is often marked by a color change from gray-brown or brown to green. However, this is obviously an imprecise measurement. Measurement of oxidation-reduction potential using a platinum probe and reference electrode in sediments often yields qualitatively useful results, but cannot be relied upon as a quantitative tool (Whitfield 1974, Stumm and Morgan 1981, pp. 490-497). Interstitial oxygen has been measured by recent investigators (Revsbech and others 1980, Revsbech 1983, and Van der Loeff and Lavaleye 1986). The elegant

method of Revsbech (1983) provides detailed interstitial gradients of dissolved oxygen using microelectrodes inserted into sediment. With additional development these techniques may become usable for routine analysis (Helder and Bakker 1985). However, even with improved techniques for oxygen determination, nitrate measurements retain value. This is because nitrate is not present as a potential contaminant in air, and more important, because porewater oxygen frequently becomes depleted well above the sediment zones in which metals can be reduced (Froelich and others 1979).

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CHAPTER 9

E_h and pH

Introduction

E_h (oxidation-reduction potential) and pH (hydrogen ion activity) are key variables in defining the geochemical environment of any seafloor area. Where inferrable (accurate determinations are difficult), they are indicators of the types of reactions that are taking place, and also allow prediction of the rate of these reactions and the products. E_h and pH also influence a sediment's capability to retain certain radionuclides.

The methods described herein may be used to determine the E_h and pH of a moist sediment sample. They are both nondestructive tests, and can be used on small sediment samples. These two tests are often linked because they employ similar instrumentation and are performed in a similar manner. Also, it may be convenient to conduct E_h and pH tests in conjunction with the test for nitrate (see Chapter 6).

E_h

The oxidation-reduction potential (E_h), as measured by this method, is defined in ASTM definition D-1129 (ASTM 1982) as the electromotive force developed by a noble metal electrode immersed in the sample and referred to a hydrogen electrode.

In a simple, reversible reaction at equilibrium, E_h is given by the Nernst equation:

$$E_h = E^O = + \frac{RT}{NF} \ln \frac{[A]^a [B]^b}{[C]^c [D]^d}$$

where R is the gas constant, T is the absolute temperature in degrees Kelvin, N is the number of electrons exchanged in the reaction equation, F is the Faraday constant, and E^O is the standard potential of the reaction in volts. A and B are the oxidized species and C and D are the reduced species. E^O is related to the Gibbs free energy of the reaction.

In practice, the E_h is measured as the potential developed between a reference electrode and a noble metal electrode, typically platinum. This oxidation-reduction potential is related to the standard hydrogen cell which is the hydrogen gas-hydrogen ion couple (Langmuir 1971).

Procedure

Most laboratory pH meters are suitable for E_h measurements when using the millivolt scale and the appropriate electrode. Typically, a combination electrode containing both the platinum and reference electrode is desirable. It is convenient to have a probe that has a plastic body and is easily cleaned for shipboard measurements. A battery-operated meter is preferred.

Several solutions can be used as standards to calibrate E_h measurements, many of which use the Fe^{++}/Fe^{+++} couple. The redox standard solution recommended in ASTM D-1498 is prepared as follows:

Dissolve 39.21 g of ferrous ammonium sulfate, 48.22 g of ferric ammonium sulfate and 56.2 mL of sulfuric acid in water and dilute to 1 liter. Using a platinum probe normalized to the hydrogen electrode (see section on calculations), the E_h should read +675 mV.

Three other reference solutions are also available. Two are recommended by the manufacturers of the Orion redox electrodes (Orion Research, Inc. 1978). Another, and perhaps the most commonly used, is Zobell's solution (Langmuir 1971).

Make sure that the probe is filled with the fresh solution recommended by the manufacturer. Rinse the probe with flowing distilled water from a squeeze bottle and blot the water on the probe with laboratory wipes. Do not rub the probe because this may generate a static electric charge.

Place the probe into the standard solution, agitate the solution until the E_h reading begins to stabilize, and then let it rest. Adjust the meter to the millivoltage of the standard. Rinse the probe as before and insert it about 1 cm into the moist sediment sample. Allow the meter to stabilize and record the value, including the sign, to the nearest 10 mV. If the reading is unstable, slight movement of the probe may help. Remove the probe and rinse. When storing the probe it should either be kept in distilled water or the filling solution should be drained.

Condition of the sediment sample is of extreme importance to this measurement. The sample must be absolutely fresh and must not have been exposed to air. The test has no thermodynamic validity in the presence of oxygen. However, it may still have qualitative value, so analysis should be performed immediately upon retrieval. If practical, use a core liner in which you have drilled holes large enough for the probe to pass through. Seal the holes with duct tape prior to sampling. These can be slit upon retrieval and the probe inserted for the measurement.

The meter-read value for E_h is a redox potential specific to the probe, reference electrode, filling solution and the sample. By convention, this value is normalized to the hydrogen electrode for each probe and filling solution by the probe manufacturer. The calculation is:

$$E_{NHE} = E_{obs} + E_{ref}$$

where E_{NHE} is the oxidation-reduction potential of the sample relative to the normal hydrogen electrode; E_{obs} is the potential developed between the platinum electrode and the reference electrode, and can be observed at the meter; and E_{ref} is the potential developed by the reference electrode relative to the normal hydrogen electrode. E_{ref} is a constant for the probe and filling solution and is provided by the probe manufacturer.

Quality assurance

Electrochemical analysis of E_h in natural systems has within it inherent sources of error that limit its usefulness to that of a semiquantitative method. It can be used to determine general redox regimes in sediment, and in many cases this is probably adequate.

In most natural water systems, there are generally multiple redox reactions occurring simultaneously. The measured potential is the sum of these reactions. The redox potential observed is therefore a mixed potential. Moreover, concentrations of reactants participating in redox reactions are often low and not at equilibrium. This causes drifting of measurements as well as uncertainities in identifying the reactions that dominate the system (Lindberg and Runnelis 1984).

Redox reactions in sediment are somewhat less problematical because concentrations of elements involved in redox reactions are typically higher in sediment than in water. Also, biological action in the sediment often produces a relatively broad range of E_h values that make E_h changes more obvious. For example, the upper few centimaters of sediment may well be ventilated by bioturbation while just below this upper layer, bacterial action causes a zone of sharply decreasing E_h.

A major source of potential error in electrochemical measurement is fouling of the platinum electrode, particularly over a series of many analyses. Oxygen can poison the reactive surface of the electrode by forming oxides or hydroxides of platinum. H_2S, H_2, CH_4, CO, and films of organic material and ferric oxhydroxides are all reported to interfere with E_h measurements (Langmuir 1971).

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Electrodes can be cleaned in several ways. ASTM D-1498 recommends immersion in warm aqua regia for one min (ASTM 1982). Others recommend first soaking the electrode in detergent solutions, then cleaning the platinum with scouring powder or a very fine abrasive such as jeweler's rouge (Langmuir 1971).

Temperature differences between the sediment being analyzed, the probe, and the reference standard may cause drifting of measured values. This effect is typically small, perhaps 15 mV between 20 °C and 5 °C.

Cost analysis

COST PER ANALYSIS AT BATCH RATE $ 10
##

pH

The pH of a solution is a measure of the hydrogen ion activity therein and is expressed as:

$$pH = -\log_{10}[H^+]$$

In practice, however, pH is not a direct measure of $[H^+]$; rather, it is determined electronically by reference to one or two (preferable) standard buffer solutions that ideally are near or bracket the pH of the unknown solution. This is necessary because, unless the solutions are diluted and composed of simple electrolytes, the liquid junction potential and individual ion activities cannot be evaluated easily and, therfore, a rigorous determination of $[H^+]$ cannot be made (Bates 1973). Seawater and, thus, the interstitial water of nearly all surficial marine sediments, is not a dilute solution. Such waters typically have ionic strengths well above that of a "dilute" solution ($I = 0.7$ vs. I equal to or less than 0.1). Accordingly, comparative measurements based on buffers and reference potentials are the operational norm for seawater and seawater-related solutions as well as most other natural aqueous solutions.

pH is commonly determined by observing the potential difference between a glass electrode and a reference electrode in a test solution. In effect, a pH meter is a specially calibrated voltmeter that is connected to paired probes or a combination probe. Thus, in operation, pH is defined as a voltage measurement made on cells of the type

glass electrode   solution (X)   KCl(aq)   reference electrode

in which solution (X) is either a buffer solution of known pH (for meter calibration) or the test solution of unknown pH. Skirrow (1975) and Stumm and Morgan (1970) give details of test conventions and pH theoretical considerations.

Procedure

This method requires a pH meter, preferably portable. A glass combination electrode should replace the noble-metal combination electrode used for E_h measurements. Standard buffer solutions are required for calibration and should generally encompass a range from pH 7 to 10. Proceed as follows:

1. Sediment samples, ideally, should be tested as soon as possible after retrieval. To facilitate this, prepare core liner in which holes have been drilled at suitable intervals before coring operations begin. Make sure the holes are large enough to accomodate the probe. Tape should be used to cover these holes during sampling. The tape can be slit or removed to allow measurement. Subcores of box cores can also be taken in this specially prepared liner.

2. Fill the pH probe with fresh filling solution as recommended by the manufacturer (Note: permanently filled probes are available, but are generally less stable and less accurate [at +/- 0.03 pH units] than a refillable type [accuracy +/- .02]).

3. Connect the probe to the meter and ascertain that all functions are normal.

4. Let the probe equilibrate in fresh seawater for at least 1 h before performing the analysis. The seawater should be kept at a temperature that is close to that of the samples, which, because the samples are retrieved from water depths greater than 4000 m, will be approximately 1-2 ^{o}C. The standard buffers should be at a similar temperature.

5. Calibrate the pH metar by first setting the temperature compensation adjustment. This will probably be in the range as stated above. Assuming buffer solutions of approximately pH 7 and 10 are selected, measure the pH of the "pH 7" buffer and adjust the meter to read the buffer value (make sure that the actual buffer value used is corrected for the cold temperature). Similarly, measure the pH of the "pH 10" buffer. If necessary, adjust the "slope" so the meter reads the proper, temperature-corrected value for this buffer. Repeat both measurements and record the results. Always rinse the probe carefully between measurements and dab it dry with soft paper. Do not wipe the probe as this may cause a static electric buildup on its surface.

6. Slit or remove the tape covering the predrilled hole and insert the probe about 2 cm into the sediment. Allow the reading to stabilize and record the results.

7. Rinse the probe with clean seawater before proceeding with other measurements.

8. At the end of the sequence of measurements, repeat measurements of the two standard buffer solutions and record the results.

9. Correct, if necessary, the sample pH values in accordance with the change of buffer values.

Quality assurance

Measurement of pH in marine waters can have a high degree of precision. In fact, according to Strickland and Parsons (1968), a precision of +/- 0.03 units should be obtainable and may actually be surpassed if proper technique and precautions are exercised. Of particular note in this regard are temperature effects, use of reliable buffer solutions, and probe maintenance.

Temperature affects pH in two ways. It can change the electrode potential and it can change the ion activity within the test solution. Both of these problems may be avoided if the sediment pore water (i.e., the test solution), the probe, and the standards are at the same temperature. It is also important to calibrate the pH meter by setting the temperature compensation control. It is desirable and common to measure pH immediately upon sample retrieval; temperature should be measured at that time on at least one sample from a given area and the compensation set accordingly (probably at 1-2 $^{\circ}C$, again assuming sediment samples are recovered from greater than 4000 m water depth). The probes and standard solutions should be kept under refrigeration at a temperature that matches the measured temperature. Although equations are available to correct a pH value to its in situ equivalent, room temperature equilibration of all components is not recommended because of the potentially adverse effects on other measurements.

Using fresh buffer solutions of appropriate values is essential for quality pH measurements. Also, the presence of CO_2 or other contaminants may alter the buffer pH value unacceptably. The National Bureau of Standards has certified nine standard buffers and provides information on the preparation and characteristics of buffer solutions. Commercially available buffers are generally accurate to +/- 0.01 pH units. Numerous publications are available that provide practical information on buffers (e.g., Beckman 1983).

Appropriate probe maintenance is also essential. Although there are many possible reasons for a slow response, a long stabilization time or inordinate drift, most of the time the problem can be traced to an electrode defect. The chance of developing a probe problem is particularly high during shipboard work because the probes are inserted directly and repeatedly into the sediment, which can lead to clogging of the fibrous reference electrode, or if H_2 is present, can lead to poisoning of the electrode. Accordingly, probes should be constantly tested and rejuvenated, unclogged, or replaced as necessary. The shipboard environment is generally harsh on probes and electronic systems in general, and care should be taken to ensure that all equipment is maintained and stored properly and that the pH meter is properly protected from salt air or physical abuse.

Because cores undergo a substantial reduction in ambient pressure as they are brought to the surface, questions have arisen concerning the possible effect of outgassing on pH; that is, as pressure is released, gases usually dominated by CO_2 are lost, affecting the pore fluids of core, especially at the insert hole for the probe. Loss of CO_2 causing increase in pH can occur even when CO_2 is not saturated in situ, if methane is lost, sweeping other gases with it. The likelihood of spurious results increases as the pressure differential between sea floor and shipboard increases. When shipboard pH measurements are made, investigators should be aware of this possible outgassing and its effect on pH values.

Cost analysis

COST PER ANALYSIS AT BATCH RATE $ 10
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CHAPTER 10

TOTAL ORGANIC CARBON

Introduction

The organic content of marine sediments reflects the chemical and physical conditions of the depositional and postdepositional environment. Many geochemical studies routinely measure organic carbon as an indicator of the amount of biogenic matter in sediment samples. Because inorganic phases of carbon are present in varying amounts, usually in the form of carbonates, analytical techniques must be used to differentiate between the organic and inorganic phases. Two methods for the analysis of organic carbon in marine sediments are presented here, and the analytical procedures, accuracy, and applicability of the methods are discussed.

Test Method A

Procedure

The first method of organic carbon analysis involves high temperature combustion using a LECO Wl2, model 1761-100, carbon analyzer on samples from which the inorganic carbon (carbonate carbon) has been removed. Removal of carbonate (pretreatment) is accomplished by using either wet or dry leach techniques.

Wet leach pretreatment using HCL (10 percent by volume)

1. Samples to be analyzed should be dried thoroughly in an oven at approximately 90 $^{\circ}$C and then ground to homogeneity (fine powder) using an agate mortar and pestle. There should be no discernable differences in texture or color after grinding. Samples can be transferred to appropriately sized glass vials for drying and storage.

2. Redry samples for about 1 h at 90 $^{\circ}$C, then transfer to dessicator and allow to cool before weighing.

3. Weigh between 0.1 and 2.5 g of sediment into acid-cleaned 50-ml beakers (which should be purified in a muffle furnace at 500 $^{\circ}$C to ensure against contamination). Samples that contain relatively high C content (3 to 7 percent) require less material; samples with high $CaCO_3$ content require the most. Samples should be weighed to four decimal places and the weights recorded. Beakers should be labeled carefully before weighing.

4. Prepare a 10 percent (by volume) HCl solution (1.2 N), and place samples on a tray in a frame hood. Carefully add 10 ml of acid to each beaker. Care must be taken with carbonate-rich samples to avoid fizzing. The samples are allowed to remain in a fume hood overnight or until no further reaction is visible.

5. Rinse sample residues carefully onto pre-ashed glass-fiber filters (47-mm diameter, 0.4-micron opening) and heat them to 500 °C for 1 h in a muffle furnace. Use an all-glass Millipore filtering assembly connected by a trap to a vacuum pump. Use only distilled water, which has been prefiltered, to rinse, and be sure to rinse any sediment from sides of glass funnel.

6. After rinsing acid from sample, fold filter in half twice using forceps. Transfer to a porous LECO combustion crucible. Cap with aluminum foil and label. Record the number next to the appropriate sample.

7. Place crucibles in the oven to dry and desiccate until you begin to run the analysis using the LECO Carbon Analyzer previously described. Standards should always be run whenever the combustion chamber is cleaned or traps in the sample lines are changed.

Dry leach pretreatment

1. Sample preparation, grinding, and drying procedures duplicate those described in steps 1 through 3, of the wet leach pretreatment. However, samples may be transferred directly into LECO crucibles after weighing, or weighed directly into the crucibles themselves. Number the crucibles by scratching the surface with a metal stylus.

2. Using an empty desiccator equipped with vacuum sleeve and perforated ceramic plate, which you have first removed, add enough concentrated HCl to cover the bottom to a depth of about 1/2 inch. Replace the ceramic plate and arrange the crucibles on the bottom in a systematic fashion. Crucibles should not be capped. Close the desiccator and leave it in the fume hood for a minimum of 3 days. Always follow appropriate safety precautions. Samples may be placed on glass petri dishes for ease in transferring; otherwise, handle with forceps. In either case, wear gloves, lab coat, and safety glasses.

3. After a minimum of 3 days, remove samples from desiccator and allow to vent for about 4 h in fume hood. Then, transfer samples to a second dessicator which has been prepared in a similar way using concentrated NH_4OH. Place samples in the desiccator, cover, and allow to stand half an hour to neutralize the absorbed HCl. Dry the samples in an oven until processing, or transfer to a desiccator until LECO-WR 12 analysis. Always desiccate samples in between analyses to guard against H_2O absorption.

Total organic carbon determination

        This method of analysis utilizes the difference in thermal conductivity between two gases, CO_2 and O_2, to measure

the amount of carbon released from a sample during combustion at 1,500 $^{\circ}$C for 60 sec. The sample is combusted in an induction furnace through which purified O_2 flows at a controlled rate. The carbon is oxidized to CO_2 and the sulphur to SO_2; residual phases remain behind as oxides. A thermal conductivity cell, consisting of matched thermistors connected by a Wheatstone bridge, registers a current imbalance when CO_2 is allowed to enter the measuring cell. This current is amplified, producing a positive reading on the digital voltmeter that is proportionate to the amount of carbon in the sample. SO_2, CO_2, and combustion solids are collected by a series of traps during various phases of the operation. A detailed description of the operation of the LECO analyzer is provided in the user's manual supplied by the manufacturer.

Quality Assurance

Dry leach method of sample preparation

The dry leach method of sample preparation for organic carbon analysis has been used in a number of different sediment types. The following data (Table 7) were obtained for samples analyzed in triplicate using the dry leach method. The range of carbon values found for each suite of analyses is listed along with standard deviation. The relative standard deviation (rsd) obtained for each sample was averaged, and the mean value for each set determined.

Table 7. Precision of Method A using dry pretreatment method.

Sample Site	No. of Analyses	Range, in percent, of Organic Carbon [+/- Std. Dev.]			Mean rsd (percent)
A *	13	0.76 +/- 0.04	-	1 15 +/- 0.33	+/- 0.76
B *	6	3.12 +/- 0.01	-	6.82 +/- 0.01	+/- 0.87
C *	6	1.68 +/- 0.18	-	6.59 +/- 0.06	+/- 1.70
D **	3	3.50 +/- 0.21	-	4.62 +/- 0.42	+/- 0.62
E **	7	0.50 +/- 0.004	-	0.72 +/- 0.014	+/- 0.84

Notes to Table

  rsd = (standard deviation/percent organic carbon) x 100.

           A = COST well No. 1 (Gulf of Mexico)
  B = Cariaco Trench   C = New York Bight
  D = Lydonia Canyon axis   E = Georges Bank shelf

   * = Whelan, J. and Pratt, M. Unpublished data, Woods Hole
          Oceanographic Institution, Woods Hole, MA

  ** = sediment trap samples, US Geological Survey, Woods Hole, MA

Wet leach method of sample preparation

Ten sediment trap samples from the axis of Lydonia Canyon on Georges Bank were analyzed in triplicate after carbonate had been removed by wet leaching. Organic carbon percentiles for these samples ranged from 2.78 +/- 0.01 to 4.00 +/- 0.14; mean rsd was +/- 1.05 percent.

The range, sensitivity, and accuracy of the LECO analyzer on 1-g samples, as reported by the LECO Corporation 1986 brochure, is listed in Table 8. The regular range is satisfactory for most carbon determinations

Table 8. Range, sensitivity, and accuracy of LECO analyzer.

Range	Sensitivity	Accuracy
Regular (0.010 - 5.000 % C)	0.001 % C	+/- 0.002 % C or 50% of carbon present
Low (0.005 - 0.200 % C)	0.0001 % C	+/- 0.0005 % C at lower levels to +/- 0.002 % C at upper levels

Cost Analysis

Test Method A is based on use of a LECO-WR12 carbon analyzer. Unit cost for batch processing depends on pretreatment procedures. Time for preparation and analysis is 0.5 - 1 h per sample.

COST PER ANALYSIS AT BATCH RATE $ 30 (wet leach)
                                         $ 20 (dry leach)

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Test Method B

Procedure

The amount of organic carbon in sediments and sedimentary rocks is determined by calculating the difference between total carbon (TC) and carbonate carbon (IC) contained in a sample. Total carbon is determined by using a Perkin-Elmer High Temperature Combustion Elemental (CHN) Analyzer; CO_2 is determined using a Coulometrics Inc. model 5011 coulometric titrator, (Engleman 1985, in press).

Total carbon

Samples to be analyzed are dried, thoroughly ground, and redried before weighing. A 1- to 2-mg sample is weighed on a microbalance and transferred to a quartz combustion tube for analysis by the CHN elemental analyzer. A complete description of instrument operation is available in the user's manual, and will not be given here. However, the analyzer works on the same principles as the LECO-W12 described previously. Acetanalide standards (71 percent TC) are used to calibrate the instrument; the relative standard deviation (rsd) is +/- 0.3 percent C (Brown, F., personal communication 1986).

CO_2 analysis

This method of analysis is based on the exact measurement of the quantity of electricity that passes through a solution during an electrochemical reaction. Between 10 and 100 mg of sample (more if carbonate content is high) are weighed into porcelain crucibles and transferred to the reaction tube. The tube is attached to the coulometer and 5 ml of 2N perchloric acid is added; the tube is heated. The carrier gas (air), which is scrubbed with KOH to remove CO_2, passes through the tube and carries the evolved CO_2 through a Ag_2SO_4 scrubber to remove chlorine and sulphur. The CO_2 is bubbled into the coulometric cell, which contains a partially aqueous medium containing ethanolamine and a colorimetric indicator. The CO_2 is quantitatively absorbed and converted to dioxyethylcarbamic acid by the ethanolamine. The coulometer electrically generates enough base to return the indicator solution to the starting point. The starting and end points are determined photometrically. Because the coulometer is electronically calibratad, empirical calibration on the basis of carbon dioxide standards is not necessary. However, it is recommended that sediment standards be prepared and routinely analyzed at the beginning and end of a run.

Quality Assurance

Method accuracy is +/- 0.4 percent CO_2 (Zoanne Brown, USGS Analytical Laboratories, personal communication 1985) based on replicate analyses. Engleman and others (1985) report a difference between within-day and day-to-day precision of approximately 5 percent rsd (relative standard deviation) or less over a concentration range of 0.01 - 36 percent CO_2 using the coulometric titrator.

Cost Analysis

Test method B is based on use of a coulometric titrator. Time for preparation and analysis is 0.5 - 1 h per sample.

COST PER ANALYSIS AT BATCH RATE $ 30
##

Discussion of Methods

Various techniques for the analysis of organic carbon in soils, sediments, and sedimentary rocks have been described in the literature and the merits and disadvantages discussed. Some of these are included in the references listed below. The major difficulty encountered in any of these analyses involves the accurate separation of the inorganic (carbonate) and organic phases of carbon. Wet leach methods, followed by filtration, may result in loss of the more labile organic compounds, particularly from recent marine samples that are high in carbonate, certain soil types, and suspended-matter samples (see, Gross and others 1972, Roberts 1973, Leventhal and Shaw 1979, Froelich 1980, Weliky and others 1983). Roberts (1973) estimated that from 9 to 44 percent organic carbon was lost from recent carbonate samples when treated with various concentrations of sulfuric acid.

Preliminary comparison of the dry vs. wet leach method was made using a standard sample which contained about 40 percent carbonate and which was run in triplicate using both preparation techniques. Mean organic carbon values obtained for the dry vs. wet leach methods were 0.615 +/- 0.012 with rsd at 2.0 percent, and 0.510 +/- 0.006 with rsd of 1.2 percent, respectively (David Brewster, USGS, unpublished data 1981). The rsd of replicate analyses using different samples (sediment-trap and piston-core samples from Georges Bank) is 1.05 percent for the dry leach method and 0.84 percent for the wet leach method. However, more detailed comparisons need to be made. The dry leach method is not recommended for samples with a high concentration of organic-diatomaceous rich oozes or carbonate contents greater than 60 percent (Jean Whelan, WHOI, personal communication 1985). For this level of carbonate, method II might be preferable.

In summary, the size and composition of the sample are important when selecting an appropriate method of analysis. If sample size is small, the CHN analyzer or Coulometric method may be more suitable. If the organic content is extremely low and the carbonate content high, methods that require more time-consuming and sophisticated techniques, such as discussed by Froelich (1980), may be required.

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GEOTECHNICAL METHODS

CHAPTER 11

WATER CONTENT

Introduction

The water content, defined as the mass of water (including dissolved components such as salt) divided by the mass of soil solids, is one of the most important and fundamental soil parameters. It is also one of the simplest to determine. The water content can indicate possible grain sizes of a sample because clay particles tend to adsorb water to their surfaces. For instance, a high water content typically indicates that a sediment has a high clay content. Some clay minerals, such as montmorillonite (smectite), have a greater tendency than others to attract water particles (Lambe and Whitman 1969, p. 44). A low water content, on the other hand, may mean that a coarser grain size is present or that a clay has been heavily loaded, which caused the adsorbed water to be squeezed out. When compared to other measured properties such as Atterberg limits, water content can be used to predict certain engineering behavior or may be evidence that particular geologic processes have occurred. Water content is used in many phase relation equations and is related to the shear strength of a saturated clay (Lambe 1951, p. 8).

Procedure

Applicable ASTM standard: D2216-80, Standard method for laboratory determination of water (moisture) content of soil, rock, and soil-aggregate mixtures (ASTM 1987, pp. 355-358).

1. Select a representative specimen that has a mass of at least 25 g. If a discontinuity or change in sediment type is encountered at a particular level, representative specimens should be obtained from each material. Spacing between specimen subsampling depends on the overall test-program objectives and should be specified as an appropriate interval; e.g. 10 cm. If a sample had previously been bagged, thoroughly remold the sediment with a spatula before obtaining a water content specimen.

2. Record the cruise and core identifiers, sample interval, water content jar identifier, and mass of a clean dry water content container.

3. Place the moist specimen in the container and determine the mass of the container plus moist material by using a balance that has a precision of +/- 0.01 g. Record the combined mass on a data form (e.g., Fig. 16).

WATER CONTENT

Cruise/Project:_____ Date:_____ Initials:_____

Oven:_____ Oven Temperature:_____ Drying Time:_____

Salinity Correction (ppt):_____ Comments:_____

Dish No.	Mass Dish + Wet Sed. (g)	Mass Dish + Dry Sed. (g)	Mass Dish (g)	Mass Water (g)	Mass Dry Sed. (g)	Water Content (%)	Corr. Water Content (%)

Figure 16. Typical water content data form.

4. Place the sample and container into a drying oven that can maintain its drying temperature within +/- 5 $^{\circ}$C. Depending on the type of sediment being dried, an oven temperature between 60 and 110 $^{\circ}$C should be used. Geotechnical testing laboratories often use a temperature of 105 $^{\circ}$C (Lambe 1951, p. 10), however, an oven temperature of 60 +/- 5 $^{\circ}$C may be more appropriate for materials containing significant amounts of hydrated water or organic material (Liu and Evett 1984, p. 7).

5. After the material has dried to a constant mass, remove the container from the oven (typically 8 to 24 h).

6. Immediately place the hot container into a desiccator to cool.

7. When the sample has cooled to a temperature at which it can be handled easily, place the container and sample on the balance to determine the combined mass of the container and dry sediment. Record the results. The dried water content sample can be saved for future grain specific gravity testing. The dried sample should not be used for grain-size analysis or x-ray diffraction studies.

8. Subtract the mass of the container and dried sediment from the mass of the container and wet sediment to obtain the mass of water without dissolved salt.

9. Determine the mass of dried sediment and salt precipitate by subtracting the container mass from the combined mass of the container and dried material.

10. The water content of the specimen (w) uncorrected for salt content in the pore fluid, can be determined from the following equation:

$$w = \frac{\text{mass of the water}}{\text{mass of the dry sediment and salt}}$$

11. The water content (w_C) corrected for salt in the pore fluid, can be determined from Table 9 (assuming a salinity of 35 ppt). Find the appropriate percentage in the right column, and add it to the uncorrected water content. For example, if the uncorrected water content value was 95 percent, 7 percent should be added, producing a corrected water content of 102 percent. The corrected water content can also be determined from the following equation using any salinity value:

$$w_C = \frac{\left(1 + \dfrac{S}{1000-S}\right) M_W}{M_S - \left(\dfrac{S}{1000-S} \times M_W\right)} \times 100$$

where: w_c = water content (in percent) corrected for a particular salinity value,
  S = salinity (in ppt),
  M_w = mass of water without salt, and
  M_s = mass of sediment including salt.

Table 9. Corrections to natural water content within a subsample to account for a salinity of 35 ppt in the pore water.

Uncorrected natural water content (percent)	Add (percent)
less than 12	0
13 to 31	1
32 to 46	2
47 to 59	3
60 to 70	4
71 to 81	5
82 to 90	6
91 to 99	7
100 to 108	8
109 to 116	9
117 to 123	10
124 to 130	11
131 to 137	12
138 to 144	13
145 to 150	14
151 to 156	15
157 to 162	16
163 to 168	17
169 to 174	18
175 to 179	19
180 to 185	20
186 to 190	21
191 to 195	22
196 to 200	23

12. The report (data sheet) should include the following: water content of the specimen to the nearest 0.1 or 1 percent, depending on the purpose and required precision of the test; indication of test specimen having a low mass (below 25 g); indication of test specimen containing more than one soil type (layered, etc.); indication of any material (size and amount) removed from the test specimen; and, the method of drying if different from oven drying at 110 +/- 5 °C

Comments

An accurate determination of water content depends on adequate sampling, handling, shipping, and storage of core sections or water content samples (see Chapter 2). Leakage of

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pore water must be prevented, as must compaction of unsampled sediment cores still within liners. Core sections or sample bags should be well sealed.

Water contents must be corrected for the salt that precipitates out of the pore water during drying because corrections can exceed 10 percent of the actual water content value.

The equation used to determine water content must always be stated because some investigators define it as mass of water (including salt) divided by the total sample mass. Using that definition, the water content must be less than 100 percent, whereas the definition in this section allows the water content to exceed 100 percent.

Quality Assurance

Although ASTM (1987) has not yet developed requirements for the precision and accuracy of this test method, Bennett and others (1970) estimated that the precision was +/- 1 percent. The method is suitable for all marine sediments, although great care must be taken in some sediment types (e.g., sands) and in surface sediments to ensure that the data represent the in situ conditions.

Cost Analysis

Time required for each water content analysis (not including drying or cooling times): 10 minutes

COST PER SAMPLE AT BATCH RATE $ 4
##

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CHAPTER 12

ATTERBERG LIMITS (LIQUID AND PLASTIC LIMITS)

Introduction

The liquid limit and plastic limit (called Atterberg limits) are the two parameters used most often to distinguish the boundaries between the consistency states of fine-grained soils. The liquid limit is the water content that separates liquid- from plastic-behaving remolded sediment, and the plastic limit separates plastic from semisolid behavior. Therefore, if the water content is above the liquid limit, the remolded sediment will behave like a liquid; if the water content is below the liquid limit, but above the plastic limit, the remolded sample will exhibit plastic behavior.

The Atterberg limits are very useful parameters because they indicate the water contents over which sediment behaves plastically. Liquid and plastic limits are related to the amount of water that is attracted to the surfaces of the individual sediment particles. Nonplastic behavior is typically exhibited by predominantly coarse-grained material. Typically, the higher the clay mineral content of a sediment, the greater will be the amount of adsorbed water on the clay particles and, hence, the higher the Atterberg limits.

Other sample parameters that can be determined from Atterberg limits include the plasticity index (I_p) which is the difference between the liquid limit and plastic limit and the liquidity index (I_L) [(natural water content minus plastic limit) + I_p], which relates the in situ water content to the Atterberg limits. The latter is useful for estimating approximate sediment stress histories. The plasticity index is often plotted versus liquid limit on a plasticity chart (Fig. 17); the location of the data indicates what type of sediment is present and also the amount of compressibility that can be expected to follow engineering-type loading (Peck and others 1974, p. 22).

Two methods of determining the liquid limit are currently in use. Within the United States, the ASTM method of using a brass drop cup is more popular. Elsewhere, however, the fall-cone method prevails. Some data exist that indicate better precision can be obtained with the fall-cone method (Head 1980).

Bentonite
(Wyoming)

Volcanic clay
(Mexico City)

Line "A"

Various types
of peat

Organic silt and clay
(Flushing meadows, L.I.)

400
300
200
100

0   200   400   600   800

Liquid limit

Sodium
Montmorillonite
LL = 300 to 600
PI = 250 to 550

70

60

50

CH   "A" line

Expansive soils
(Ref. 14a)

Glacial clays

Diatomaceous
earth

Red tropical
laterite clays

CL

Kaolin and alluvial clays

Micaceous silts

Loess

MH and OH

CL-ML

ML and OL

Plasticity index, %

50
40
30
20
10
7
4
0

10   20   30   40   50   60   70   80   90

Liquid limit

Figure 17. Plasticity chart showing location of some types of soil (Hunt, 1984, p. 148). The following abbreviations are used; C: clay; H: high plasticity; L: low plasticity; LL: liquid limit; M: silt; O: organic; and PI: plasticity index.

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Liquid Limit

Test Method A: Casagrande Drop Cup

In the following method, the liquid limit is defined as the water content at which both sides of a remolded pat of soil, placed in a standard cup and cut by a groove of standard dimensions, will flow together at the base of the groove for a distance of 13 mm (0.5 in) when the soil is subjected to 25 shocks from the cup being dropped 10 mm in a standard liquid-limit apparatus operated at a rate of 2 shocks per second.

Procedure

Applicable ASTM Standard: D4318-84, Standard test method for liquid limit, plastic limit, and plasticity index of soils (ASTM 1987, pp. 763-778).

1. Obtain a representative sediment sample. Note: although ASTM recommends removing material retained on a No. 40 sieve (425 micron), that practice artificially biases the test results to indicate that a more plastic material is present.

2. After calibrating the apparatus, place a portion of the remolded soil in the cup of the liquid limit device (Fig. 18) at the point where the cup rests on the base. Squeeze it down, and spread it into the cup to a depth of about 10 mm at its deepest point, tapering it to form an approximately horizontal surface. Take care to eliminate air bubbles from the soil.

3. Form a groove in the soil by drawing the tool, beveled edge forward, through the soil. When cutting the groove, hold the grooving tool against the surface of the cup and draw it in an arc, maintaining the tool perpendicular to the surface of the cup throughout its movement. In soils where a groove cannot be made in one stroke without tearing the soil, cut the groove with several strokes of the grooving tool. Alternatively, cut the groove to slightly less than required dimensions with a spatula and use the grooving tool to bring the groove to final dimensions. Exercise extreme care to prevent sliding the soil pat relative to the surface of the cup.

4. Verify that no crumbs of soil are present on the base or the underside of the cup. Lift and drop the cup by turning the crank at a rate of 1.9 to 2.1 drops per second until the two halves of the soil pat come in contact at the bottom of the groove along a distance of 13 mm (0.5 in).

DIMENSIONS

LETTER	A△	B△	C△	E△	F	G	H	J△	K△	L△	M△
MM	54 ± 0.5	2 ± 0.1	27 ± 0.5	56 ± 2.0	32	10	16	60 ± 1.0	50 ± 2.0	150 ± 2.0	125 ± 2.0

LETTER	N	P	R	T	U△	V	W	Z
MM	24	28	24	45	47 ± 1.0	3.8	13	6.5

△ ESSENTIAL DIMENSIONS
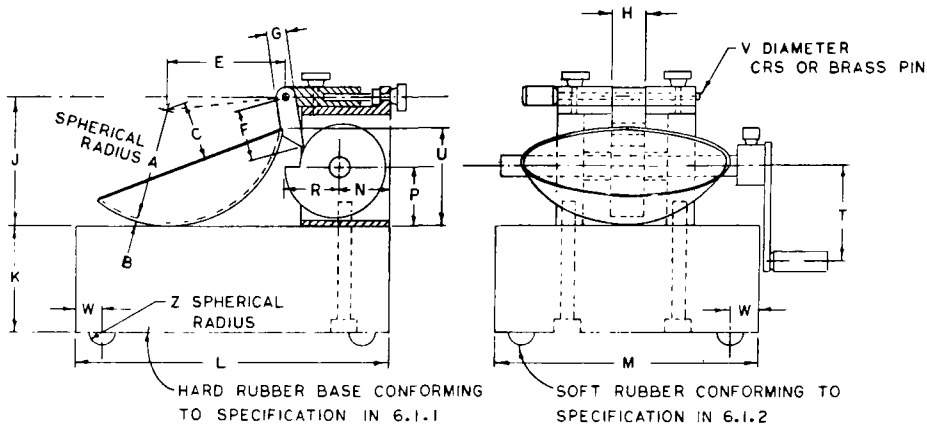
CAM ANGLE DEGREES	CAM RADIUS
0	0.742 R
30	0.753 R
60	0.764 R
90	0.773 R
120	0.784 R
150	0.796 R
180	0.818 R
210	0.854 R
240	0.901 R
270	0.945 R
300	0.974 R
330	0.995 R
360	1.000 R

Hand-Operated Liquid Limit Device

DIMENSIONS

LETTER	A△	B△	C△	D△	E△	F△
MM	2 ± 0.1	11 ± 0.2	40 ± 0.5	8 ± 0.1	50 ± 0.5	2 ± 0.1

LETTER	G	H	J	K△	L△	N
MM	10 MINIMUM	13	60	10 ± 0.05	60 DEG ± I DEG	20

△ ESSENTIAL DIMENSIONS

□ BACK AT LEAST 15 MM FROM TIP

NOTE : DIMENSION A SHOULD BE 1.9–2.0 AND DIMENSION D
SHOULD BE 8.0–8.1 WHEN NEW TO ALLOW FOR
ADEQUATE SERVICE LIFE
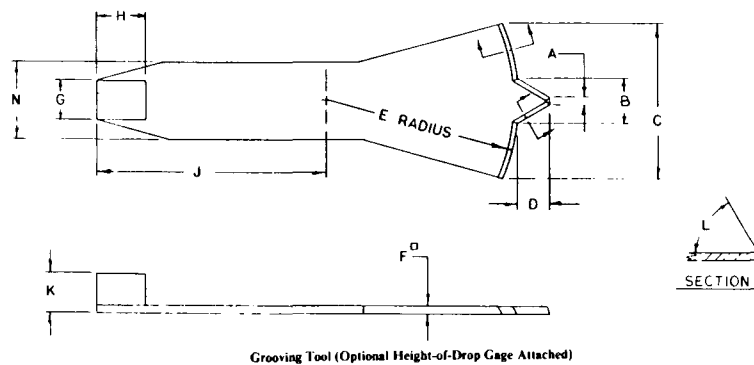
Grooving Tool (Optional Height-of-Drop Gage Attached)

Figure 18.   Mechanical drop cup liquid limit device and grooving tool (ASTM, 1987, p. 774-775).

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5. Verify that an air bubble has not caused premature closure by observing that both sides of the groove have flowed together with approximately the same shape. If a bubble has caused premature closing of the groove, reform the soil in the cup, adding a small amount of soil to make up for any lost in the grooving operation, and repeat steps 2 to 4. If the soil slides on the surface of the cup, repeat steps 2 through 4 at a different water content. If, after several trials at successively higher and lower water contents, the soil pat continues to slide in the cup or if the number of blows required to close the groove is always less than 25, record that the liquid limit could not be determined, and report the soil as nonplastic without performing the plastic limit test.

6. Remix the soil sample on the glass plate without adding to, or removing pore water from the sediment and return a pat of soil to the cup, performing steps two through five. When the operator has recorded at least two trials within one count from each other, record the number of drops, N, required to close the groove. Remove a slice of soil approximately 20 mm wide, extending from edge to edge of the soil cake at right angles to the groove and including that portion of the groove in which the soil flowed together. Place in a weighed container and cover.

7. Return the soil remaining in the cup to the glass plate. Wash and dry the cup and grooving tool prior to the next trial.

8. Remix the soil specimen on the glass plate, adding or reducing water to increase or decrease the water content of the soil and change the number of blows required to close the groove. Repeat steps two through seven for at least two additional sets of trials. One set of the trials should be for a closure requiring 25 to 35 blows; one for closure between 20 and 30 blows; and one trial for a closure requiring 15 to 25 blows.

NOTE Some investigators add saline water to the sediment or use absorbent material to remove pore water so that the salinity of the sediment is not changed.

9. Determine the water content, w_c, of the soil specimen from each trial in accordance with the prior section, making sure that the water contents are corrected, at least approximately, for salt content. Make all weighings on the same balance. Initial weighings should be performed immediately after completion of the test.

10. Plot the relationship between the water content, w_c, and the corresponding number of drops, N, of the cup on a semilogarithmic graph with the water content as the ordinate on the arithmetical scale and the number of drops as the abscissa on the logarithmic scale (Fig. 19). Draw the best-fit straight line through the three or more plotted points.

11. The test information can be recorded on a form similar to Figure 20. On the graph, the point at which the best-fit line intersects the 25-drop abscissa line corresponds with the liquid limit of the soil. Computational methods may be substituted for the graphic method. The liquid limit should be rounded to the nearest whole number.

Quality Assurance

ASTM states that no interlaboratory testing program has yet been performed to determine field-wide precision. However, they presented the precision of the test results as performed by different individuals in one laboratory.

Within Laboratory Precision for Liquid Limit

		Average Value	Standard Deviation
Soil A:	w_L	27.9	1.07
Soil B:	w_L	32.6	0.98

Cost Analysis

Time required for each drop cup liquid limit analysis (not including drying or cooling times): 1 h

COST PER SAMPLE AT BATCH RATE $ 20
##
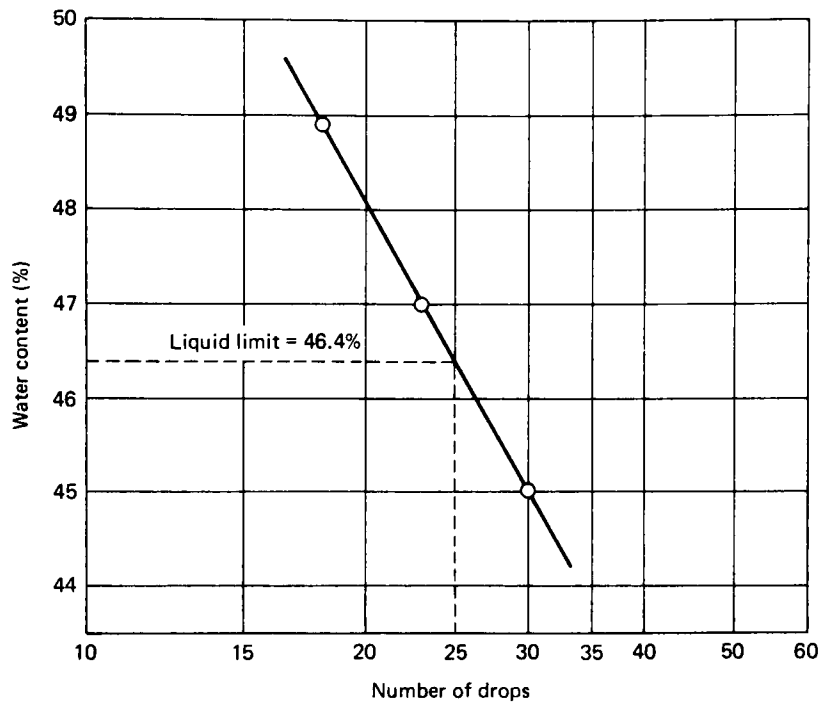
Figure 19. Water content versus number of drops from a drop cup liquid limit test (Liu and Evett, 1984, p. 34).
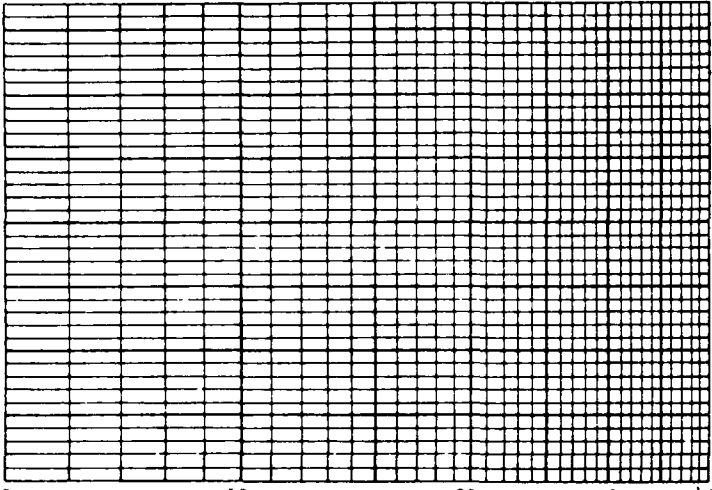
LIQUID AND PLASTIC LIMIT TESTS

Date _____

Project _____

Boring No. _____ Sample No. _____

LIQUID LIMIT

Run No.	1	2	3	4	5	6
Tare No.						
Tare plus wet soil						
Tare plus dry soil						
Water W_w						
Tare						
Dry soil W_s						
Water content w						
Number of blows						

Weight in grams

Water content, w

Number of blows

5   10   20   30   40

LL _____

PL _____

PI _____

Symbol from plasticity chart

_____

PLASTIC LIMIT

Run No.	1	2	3	4	5	Natural Water Content
Tare No.						
Tare plus wet soil						
Tare plus dry soil						
Water W_w						
Tare						
Dry soil W_s						
Water content w						
Plastic limit						

Weight in grams

Remarks _____

_____

Technician _____ Computed by _____ Checked by _____

Figure 20.   Typical liquid limit and plastic limit test data form (Dept. of the Army, 1980, p. III-19).

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Test Method B: Fall-Cone Penetrometer

In the following method, the liquid limit is defined as the water content at which a cone with specific dimensions and mass penetrates the flat surface of remolded sediment to a prescribed distance.

Procedure

Applicable standard: BS 1377, 1975, Test 2 (A); British standard test for liquid limit - cone penetrometer method, British Standards Institution, London, England.

1. Obtain a representative sediment sample.

2. Thoroughly remold the material in a large evaporating dish with a spatula.

3. Fill the metal penetrometer cup with sediment, being careful not to trap air bubbles within the sediment during the placement procedure.

4. Evenly scrape off any material above the top of the cup with a spatula or wire saw, leaving a flat sediment surface.

5. Place the sediment onto the liquid limit device making sure that the cone tip barely comes into contact with the sediment surface (Fig. 21).

6. Release the cone and allow it to penetrate the sediment for exactly 5 sec; record the penetration depth.

7. Remove the sediment cup from the device, clean the cone, and remold the sediment within the cup. Repeat steps two through six until the second penetration is within 0.2 mm of the previous depth.

8. With a small spatula, take a water content subsample from the zone adjacent to the penetration void.

9. Return the remaining sediment from the penetrometer cup to the evaporating dish. Change the water content so that three equally spaced penetrations between 10 and 30 mm are obtained.

10. Plot the water content versus penetration depth for the three trials on a data form (Fig. 22) and determine the liquid limit (corrected for salt content) related to the standard penetration depth for the particular cone in use. For example, a cone with a mass of 80.00 +/- 0.05 g

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Figure 21. Fall cone penetrometer and electric timer used for determining the liquid limit of sediment (the timer automatically stops penetration after five seconds have elapsed).

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Date _____   Sample I.D. _____   Name _____

Plasticity Index (Ip) = $W_L - Wp$

Liquidity Index (I_L) = $\dfrac{Wc - Wp}{W_L - Wp}$

Bulk Density (γt) = $\dfrac{Gs(1 + Wc/100)}{1+e}$

Void Ratio (e) = $\dfrac{Wc \times Gs}{100}$

Porosity (n) = $\dfrac{e}{1+e}$

WATER CONTENT (%)
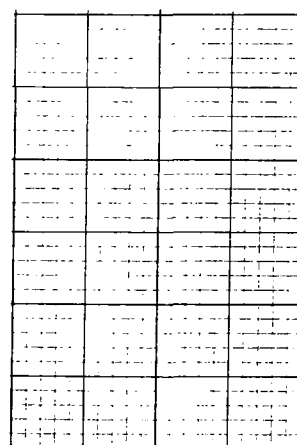
PENETRATION (mm)

10   20   30

LIQUID LIMIT

Dish #	:	:	:
Wt. Dish + Wet Soil	:	:	:
Wt. Dish + Dry Soil	:	:	:
Wt. Dish	:	:	:
Wt. Water	:	:	:
Wt. Dry Soil	:	:	:
Liquid Limit %	:	:	:
Penetration mm	:	:	:
Avg. Penetration	:	:	:

PLASTIC LIMIT

Dish #	:
Wt. Dish + Wet Soil	:
Wt. Dish + Dry Soil	:
Wt. Dish	:
Wt. Water	:
Wt. Dry Soil	:
Plastic Limit %	:

SUMMARY OF RAW RESULTS

Liquid Limit	_____
Plastic Limit	_____
Liquidity Index	_____
Plasticity Index	_____
Nat. Water Content	_____
Specific Gravity	_____

SUMMARY OF SALT CORRECTED RESULTS

****

Liquid Limit (W_L) _____	Plasticity Index (Ip) _____	Bulk Density (γ_t) _____
Plastic Limit (Wp) _____	Nat. Water Content (W_c) _____	Void Ratio (e) _____
Liquidity Index (I_L) _____	Specific Gravity (G_s) _____	Porosity (n) _____

****

Figure   22.   Typical fall-cone Atterberg limits and summary data form.

and an apex angle of 30 degrees requires a penetration of 20 mm to define the liquid limit. Round off the liquid limit value to the nearest whole number.

Quality Assurance

The precision of the fall-cone penetrometer liquid limit test is not known at the present time, however, it may be more precise than the drop cup method.

Cost Analysis

Time required for each fall cone liquid limit analysis (not including drying and cooling times): 1 h

COST PER SAMPLE AT BATCH RATE $20
##

Discussion

Head (1980) states that although the fall-cone test is no quicker to perform, it is more dependable because the test mechanics are based on the remolded static shear strength alone, without dynamic factors entering the analysis. Head also notes that the cone method produces more consistent results than the Casagrande method. Some researchers note that up to liquid limits of 100 percent, results between the two methods show little difference (Fig. 23) [Head 1980, p. 67, Wasti and Bezirci 1986].

Plastic Limit

Introduction

The plastic limit test is typically performed immediately after the liquid limit test and provides the lowest water-content value at which a soil behaves plastically in a remolded state. The plastic limit is determined by first pressing a small portion of plastic soil together, rolling it into a 3.2-mm (1/8-in) diameter thread (which gradually removes the water), and repeating the process until the thread crumbles and can no longer be pressed together and rerolled. The water content of the soil at this stage is reported as the plastic limit.

Procedure

Applicable ASTM standard: D4318-84, Standard test method for liquid limit, plastic limit, and plasticity index of soils (ASTM 1987, pp. 763-778).

1. Select approximately a 20-g representative portion of soil from the material prepared for the liquid limit test. Thoroughly remold the sample.
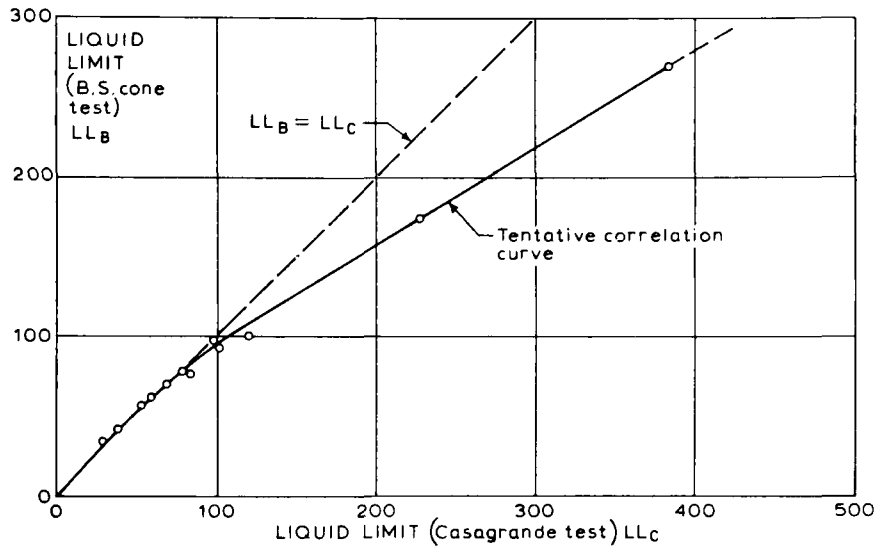
Figure 23. Correlation between fall cone and drop cup methods of determining liquid limits (Head, 1980, p. 67). The following abbreviations were used; B.S.: British standard; LL_B: liquid limit determined using the British standard; and LL_C: liquid limit determined using the Casagrande drop cup method.

2. Change the water content of the soil to a consistency at which it can be rolled by spreading and remolding continuously on a glass plate to encourage evaporation. The drying process may be accelerated by exposing the soil to the air current from an electric fan or by blotting with hard surface paper towels or high-wet-strength filter paper (to avoid adding fiber to the soil).

3. From the 20-g mass, select a 1.5- to 2.0-g portion. Form the test specimen into an ellipsoidal mass. Roll this mass between the palm or fingers and the ground-glass plate with just enough pressure to roll the mass into a thread of uniform diameter along its entire length. The thread should be further deformed on each stroke so that its diameter is continuously reduced and its length extended until the diameter reaches 3.2 +/- 0.5 mm (0.125 +/- .020 in). This should take no more than 2 min. The amount of hand or finger pressure required will vary greatly according to the soil. A normal rate of rolling for most soils should be 80 to 90 strokes per minute, counting a stroke as one complete motion of the hand forward and back to the starting position. This rate of rolling may have to be decreased for very fragile soils.

4. When the diameter of the thread is approximately 3.2 mm, break the thread into several pieces. Squeeze the pieces together, knead together, reform into an ellipsoidal mass, and reroll to 3.2 mm. Repeat this gathering, kneading and rerolling, until the thread crumbles under the pressure required for rolling and the soil can no longer be rolled into a 3.2-mm diameter thread. If crumbling occurs when the thread has a diameter greater than 3.2 mm, this shall be considered a satisfactory end point, provided the soil has been previously rolled into a thread 3.2 mm in diameter.

5. Gather the portions of the crumbled thread together and place them in a preweighed container. Immediately cover the container.

6. Select another 1.5- to 2.0-g portion of soil from the original 20-g specimen and repeat steps three to five until the container holds at least 6 g of soil.

7. Repeat the full process until a second container, holding at least 6 g of soil, is prepared.

8. Determine the salt-corrected water content, in percent, of the soil contained in the containers (refer

to that procedural section) and enter all data on a test form such as Figure 22. Plastic limit results should be rounded off to the nearest whole number. If either the liquid limit or the plastic limit cannot be determined, or if the plastic limit is greater than the liquid limit, the sediment is nonplastic (NP).

Comments

The test method for determining the plastic limit is straightforward; however, ASTM standard D4318-84 should be consulted to ensure that the rate of rolling the thread, time allowed to perform the test, etc. are properly performed. If the ASTM standard is not followed exactly (except for the removal of the 425-micron fraction), the results can be misleading. For example, a nonplastic soil can appear to exhibit slight plasticity.

Numerous investigators have found that liquid limit and plastic limit values are significantly affected by the amount of organic matter that is present in the sediment (Booth and Dahl 1986). Typically, an increase in organic content increases both the liquid and plastic limits. Therefore, organic content should be measured and reported for those sediments suspected of containing significant amounts of organic matter.

Quality Assurance

ASTM states that no interlaboratory testing program has as yet been performed to determine field-wide precision. However, the precision within one laboratory of the test method performed by different individuals is as follows

---

Within Laboratory Precision for Plastic Limit

		Average Value	Standard Deviation
Soil A:	w_p	21.9	1.07
Soil B:	w_p	20.1	1.21

Cost Analysis

Time required for each plastic limit determination (not including drying or cooling times): 30 min

COST PER SAMPLE AT BATCH RATE $10
##

References

American Society for Testing and Materials, 1987. Annual book of standards: soil and rock, building stones and geotextiles, ASTM, Philadelphia, PA, vol. 04:08, 1189 pp.

British Standards Institution, 1975. Standard test for liquid limit-cone penetrometer method, London, England.

Booth, J. S. and Dahl, A. G., 1986. A note on the relationships between organic matter and some geotechnical properties of a marine sediment, Marine Geotechnology, vol. 6, no. 3, pp. 281-297.

Head, K. H., 1980. Manual of soil laboratory testing, volume 1: soil classification and compaction tests, Pentech Press, London, England, 339 pp.

Hunt, R. E., 1984. Geotechnical engineering investigation manual, McGraw Hill, New York, NY, 983 pp.

Liu, C. and Evett, J.B., 1984. Soil properties testing, measurement, and evaluation, Prentice-Hall, Englewood Cliffs, NJ, 315 pp.

Peck, R. B., Hanson, W. E. and Thornburn, T. H., 1974. Foundation engineering, John Wiley, New York, NY, 514 pp.

US Deptartment of the Army, 1980. Engineer Manual EM 1110-2-1906: laboratory soils testing, Washington, DC, 388 pp.

Wasti, Y. and Bezirici, M. H., 1986. Determination of the consistency limits of soils by the fall cone test, Canadian Geotechnical Journal, vol. 23, no. 2, pp. 241-246.

CHAPTER 13

GRAIN SPECIFIC GRAVITY

Introduction

The specific gravity of soil is defined as the ratio of
the mass of a unit volume of a material at a stated temperature to
the mass in air of the same volume of gas-free distilled water at
a stated temperature (ASTM 1987, p. 210). The grain specific
gravity can be used, in conjunction with the salt-corrected water
content, to estimate in situ overburden stresses as well as the
possible presence of certain minerals.

Two methods are presently used to determine the grain
specific gravity. The traditional method (see A below), involves
filling a glass pycnometer with sediment and distilled water;
removing the entrapped air (possibly by boiling); cooling to room
temperature; measuring the water's temperature; weighing the
device; and finally, determining the grain specific gravity after
correcting the density of the water for temperature. A newer
method (see B) relies on a self-contained apparatus that simply
involves weighing the sample and placing it into the pycnometer to
measure volume (some devices are completely automated and measure
volumes of five samples simultaneously), and then making a simple
calculation.

Test Method A: Water-filled pychnometer

Procedure

Applicable ASTM Standard: D854-83, Standard test method
for specific gravity of soils (ASTM 1987, p. 210-213).

1. Calibrate pycnometer.

2. Place a sediment sample in the pycnometer. If a
volumetric flask is used, the sample should have a mass
of at least 25 g; if a stoppered bottle is used, the
sample should have a mass of at least 10 g.

3. Add sufficient distilled water to fill the volumetric
flask about three-fourths full or the stoppered bottle
about half full.

4. Remove entrapped air by subjecting the contents to a
partial vacuum or boiling gently for at least 10 min,
occasionally rolling the pycnometer to assist in the
removal of the air. Subject the contents to reduced air
pressure either by connecting the pycnometer directly to
an aspirator or vacuum pump, or by using a bell jar.
Note: some soils boil violently when subjected to reduced

air pressure. If that happens reduce the air pressure at a slower rate or use a larger flask. Allow heated samples to come to ambient temperature before proceeding with the analysis.

5. Fill the pycnometer with distilled water, clean the outside, and dry with a clean, dry cloth. Determine the weight of the pycnometer and contents, and the temperature of the contents. Calculate the specific gravity of the soil according to the ASTM standard D854-83 and record the information on a form similar to Figure 24. Grain specific gravity should be reported to two decimal places.

Quality Assurance

ASTM has determined the precision of the test for cohesive soils as:

	Standard Deviation	Acceptable Difference *
Single-operator precision	0.021	0.06
Multilaboratory precision	0.056	0.16

*The difference between the results of two properly conducted tests should not exceed the acceptable difference.

Cost Analysis

Time required for each test: 2 h

COST PER ANALYSIS AT BATCH RATE $40

##

Test Method B: Gas-pressurized pychnometer

Procedure

1. Grind an oven dried sample to a fine sand-sized powder using a mortar and pestle.

2. Place the sample in a small evaporating dish or water content tin and leave it in an oven at a temperature between 60 and 110 °C for a minimum of 8 h.

3. Remove the sample from the oven and let it cool to room temperature in a desiccator so that moisture in the air won't be adsorbed by any clay minerals.

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Soils Testing Laboratory
Specific Gravity Determination

Sample No. _____   Project No. _____

Boring No. _____   Location _____

Depth _____

Description of Sample _____

Tested by _____   Date _____

[A] Calibration of Pycnometer

    (1) Weight of dry, clean pycnometer, W_p _____ g

    (2) Weight of pycnometer + water, W_{pw} _____ g

    (3) Observed temperature of water, T_i _____ °C

[B] Specific Gravity Determination

Determination No.:	1	2	3
Weight of pycnometer + soil + water, W_{pws} (g)			
Temperature, T_x (°C)			
Weight of pycnometer + water at T_x, W_{pw} (at T_x) (g)			
Evaporating dish no.			
Weight of evaporating dish, W_d (g)			
Weight of evaporating dish + oven-dried soil, W_{ds} (g)			
Weight of solids, W_s (g)			
Conversion factor, K			
Specific gravity of soil $$G_s = \frac{KW_s}{W_s + W_{pw}(\text{at } T_x) - W_{pws}}$$			

Figure 24. Typical data form for grain specific gravity determined using the water filled pycnometer method (Liu and Evett, 1984, p. 23).

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4. Place the sample into a pycnometer cup of known mass and place it into the pycnometer (Fig. 25).

5. Determine the volume of the soil grains according to the manufacturer's instructions.

6. Remove the sample and cup from the pycnometer and determine the mass of the sample and cup.

7. Specific gravity is determined by dividing the mass of soil grains by the volume of soil grains and is reported to two decimal places.

8. Correct the specific gravity for salt content by using Table 10. The calculations can be made on a form similar to Figure 26. The corrected grain specific gravity can also be determined from the following equation, using any salinity or salt density values:

$$G_{SC} = \frac{M_S - \left(\dfrac{S}{1000 - S} \times w \times M_S \right)}{\left(V_S - \dfrac{\dfrac{S}{1000 - S} \times w \times M_S}{p_S} \right) p_W}$$

where: G_{SC} = grain specific gravity corrected for a particular salinity and salt density value,

M_S = mass of sediment (including salt) of pycnometer sample,

V_S = volume of sediment (including salt) of pycnometer sample,

S = pore-water salinity (in ppt),

w = water content (in decimal form) not corrected for salt content,

p_S = sea-salt density (typically 2.18 g/cm^3), and

p_W = distilled water density at a temperature of 4 °C (1 g/cm^3).

Quality Assurance

Manufacturer's listing of the accuracy of volume determination for particular pycnometers range from +/- 0.1 to 0.2 percent or +/- 0.05 cc. Check the manufacturer's information to determine the precision of a particular pycnometer.

Figure 25. Gas pressurized pycnometer.

PYCNOMETER

SAMPLE ID	WEIGHT	MEASURED VOLUME	TARE	CORRECTED VOLUME	S.G.		SALT COR. W.C.
					RAW	SALT COR	

Figure 26. Form for recording data and determining grain specific gravity by gas pressurized pycnometer.

Table 10. Corrections to add to raw specific gravity to account for a salinity of 35 ppt in the pore water.

Salt-corrected water content (percent)	Add to raw specific gravity
18 to 67	.01
68 to 116	.02
117 to 165	.03
166 to 214	.04

Cost Analysis

Time required for each test (not including drying and cooling times): 5 to 20 min.

COST PER ANALYSIS AT BATCH RATE $10
##

Discussion

The use of a pressurized gas pycnometer (Method B) is much preferred because the precision is greater and the time required to perform each test is less than that required by the ASTM method.

If using Method B, extreme care must be exercised to minimize the sample's exposure time to air after it has been removed from the oven. Some clay minerals quickly attract moisture in the air to their surfaces, thereby decreasing the measured specific gravity values.

References

American Society for Testing and Materials, 1987. Annual book of standards: soil and rock, building stones and geotextiles, ASTM, Philadelphia, PA, vol. 04:08, 1189 pp.

Liu, C. and Evett, J.B., 1984. Soil properties testing, measurement, and evaluation, Prentice-Hall, Englewood Cliffs, NJ, 315 pp.

CHAPTER 14

LABORATORY VANE SHEAR STRENGTH

Introduction

The miniature vane shear test is performed to determine
an approximate value of the undrained shear strength in
fine-grained soil. The sensitivity (that is the ratio of natural
undrained shear strength divided by the remolded undrained shear
strength) can also be calculated. The test consists of inserting
a four-bladed vane into the sediment, rotating the shaft connected
to the blades, and measuring the torque required to shear the
sediment. By assuming a particular failure surface within the
soil, the undrained shear strength (s_u) can be calculated.

Although ASTM (1987) has a standard for vane shear
testing in the field, it does not yet have one for laboratory
testing although such a standard is presently under review. The
related method D2573-72, standard test method for field vane shear
test in cohesive soil, is currently being revised. Some
information is pertinent to both types of tests.

Procedure

1. Make sure that the core section and vane shear
machine (Fig. 27) are securely positioned so that neither
will move during testing.

2. Take an initial reading on the rotation dial or set
the initial reading to 0°.

3. Insert the vane into the sediment so that the top of
the vane is about one vane height below the sediment
surface. The center of the vane should be at least 1.5
vane diameters away from any liner surface or wall.

4. Rotate the vane, or the spring top, at a rate of
90° per minute until a peak torque is reached. Record
the peak value on a data form similar to Figure 28.

5. Remove the drive belt and remold the sediment by
rotating the vane by hand rapidly through at least one
revolution. Another, more time consuming, method is to
remove the sediment and physically remold it within a
plastic bag to avoid entrapping air. Carefully replace
the sediment into a container and re-insert the vane.

6. Reattach the belt (if necessary), rotate the vane,
and read the peak torque. Record the peak value as the
remolded peak on the data form.

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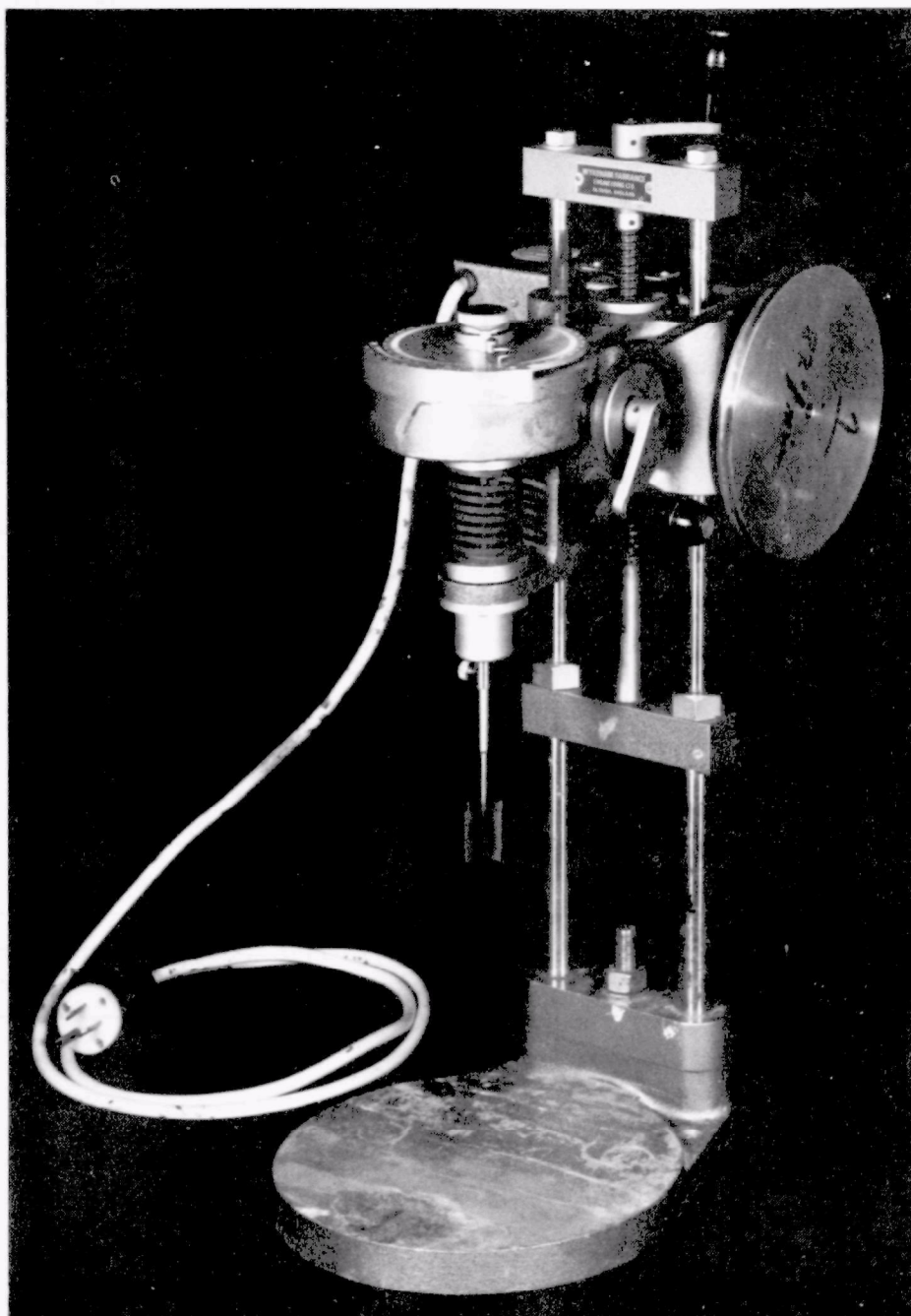
Figure 27. Vane shear machine that uses a spring to apply torque to the vane.

VANE SHEAR DATA

CRUISE _____   LAT. _____ LONG. _____   RECOVERED LENGTH _____

CORE ID _____   GEN. LOCATION _____   OPERATOR'S NAME _____

PENETRATION	SPRING SERIES AND NUMBER	NATURAL SHEAR STRENGTH		REMOLDED SHEAR STRENGTH		St (Su/Sr)	DESCRIPTION AND EVIDENCE OF DISTURBANCE
		DEGREES	Su (kPa)	DEGREES	Sr (kPa)		

Figure 28.   Typical vane shear data form.

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7. Extract the vane.

8. Remove a 10- to 20-g water-content sample from the zone where the vane test was run.

9. Insert a nonwater-absorbing plug in the resulting hole.

10. The undrained shear strength, s_u, can be determined from the following equation:

$$s_u = \frac{4T}{2\pi d^2 h + 0.667\pi d^3}$$

where: T = measured torque (determined from equipment calibration),
d = diameter of vane, and
h = height of vane.

The factor, 0.667, represents uniform end shear resistance at the top and bottom of the vane. Other assumptions regarding end shear resistance changes the factor from 0.5 for a triangular distribution to 0.6 for a parabolic distribution (Bowles 1979, p. 381).

11. Determine the water content of the sediment.

12. Record the results on a form similar to Figure 28. Shear strength values should be recorded to the nearest 0.1 kPa.

Comments

The vane shear test is relatively simple to perform. However, any of a number of operational errors can result in seriously skewed results. To keep the accuracy as high as possible, consider the following points:

(1) To ensure that undrained conditions prevail, the vane shear test should only be performed in fine-grained sediment, using a rotation rate of about 90° per min. Coarse-grained sediment should not be tested because they can lose much of their confining stress prior to testing, thereby causing laboratory strength determinations to be low.

(2) To ensure valid test results a soil must exhibit plastic behavior, contain less than 15 percent very fine sand, and must not display drainage or tension cracks during shear.

(3) Lee (1985) summarizes the current uses and limitations of the laboratory vane shear test, and suggests that plastic soils with a liquid limit above 30 percent can be tested.

(4) Be sure vane is placed in an area of the core where it will not contact any gross unconformities, i.e. clasts, shells, gravel or sand lenses. Sharp climbs in peak torque values may be an indication that the vane has contacted the liner or a clast (e.g., shell or rock fragment) within the matrix.

(5) Sediment with shear strengths greater than 100 kPa should not be tested with the vane shear machine because failure conditions deviate significantly from the assumed mode (Noorany 1985).

(6) Sample disturbance and improper storage can severely affect measured strength values. Therefore, methods that impart little disturbance must be used to obtain, transport, and store sediment cores (see Chapter 2).

Vane blade size is not very important although a blade of equal height and diameter (e.g. 12.7 mm x 12.7 mm) or one with height equal to twice the diameter is often used. In very soft sediment, a larger (e.g. 25.4 mm) blade should be used to increase the measured torque and, thereby, the accuracy of the measurement.

Most vane shear machines use a spring to apply torque to the vane. Recently torque sensors have been used to apply and measure the torque (Fig. 29). The torque sensor method possesses some advantages over the traditional method: it is able to provide a hard copy of stress versus time plot; it measures post-peak behavior; and, it turns the vane at a constant rate. Spring-mounted systems tend to turn the vane at an extremely slow rate at first, then rapidly increases the rate as failure is approached. However, few data exist to indicate that the added expense of a torque-sensor system is justified by increased accuracy.

Two other methods of rapidly determining undrained shear strength are occasionally used: the torvane (Fig. 30) and pocket penetrometer (Fig. 31). Although the torvane is typically more accurate than the pocket penetrometer, the laboratory vane shear test is superior to both and should be performed whenever possible.

Quality Assurance

Although methods to determine accuracy of the laboratory vane shear test have not been formulated, a precision of 0.5 degree of spring rotation can be obtained. However, the test must be conducted carefully because some vane shear machines have up to a 2 degree "play" that must be eliminated.
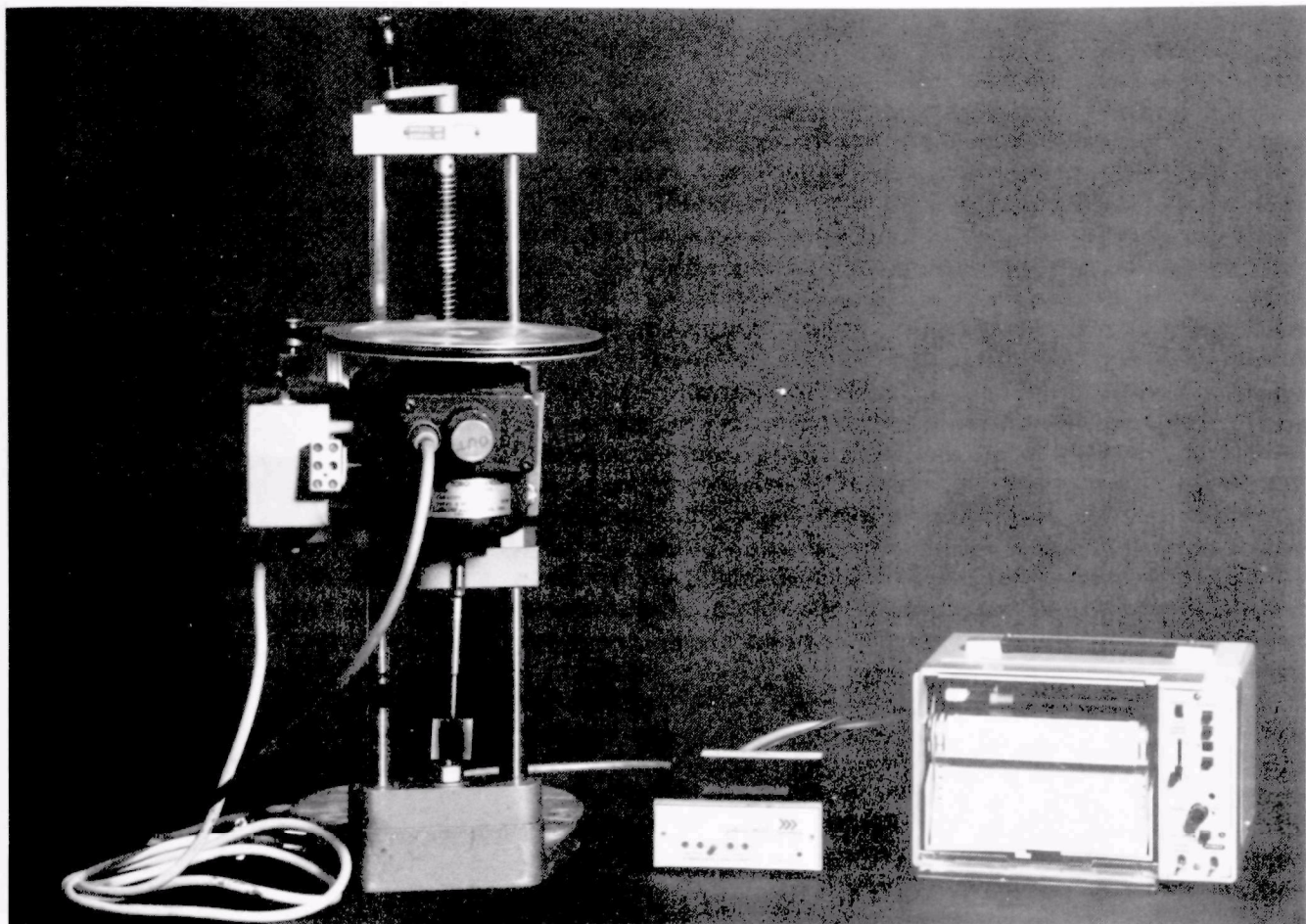
Figure 29. Vane shear machine that uses a torque sensor to rotate the vane (middle: torque sensor signal conditioner, right: strip chart recorder).

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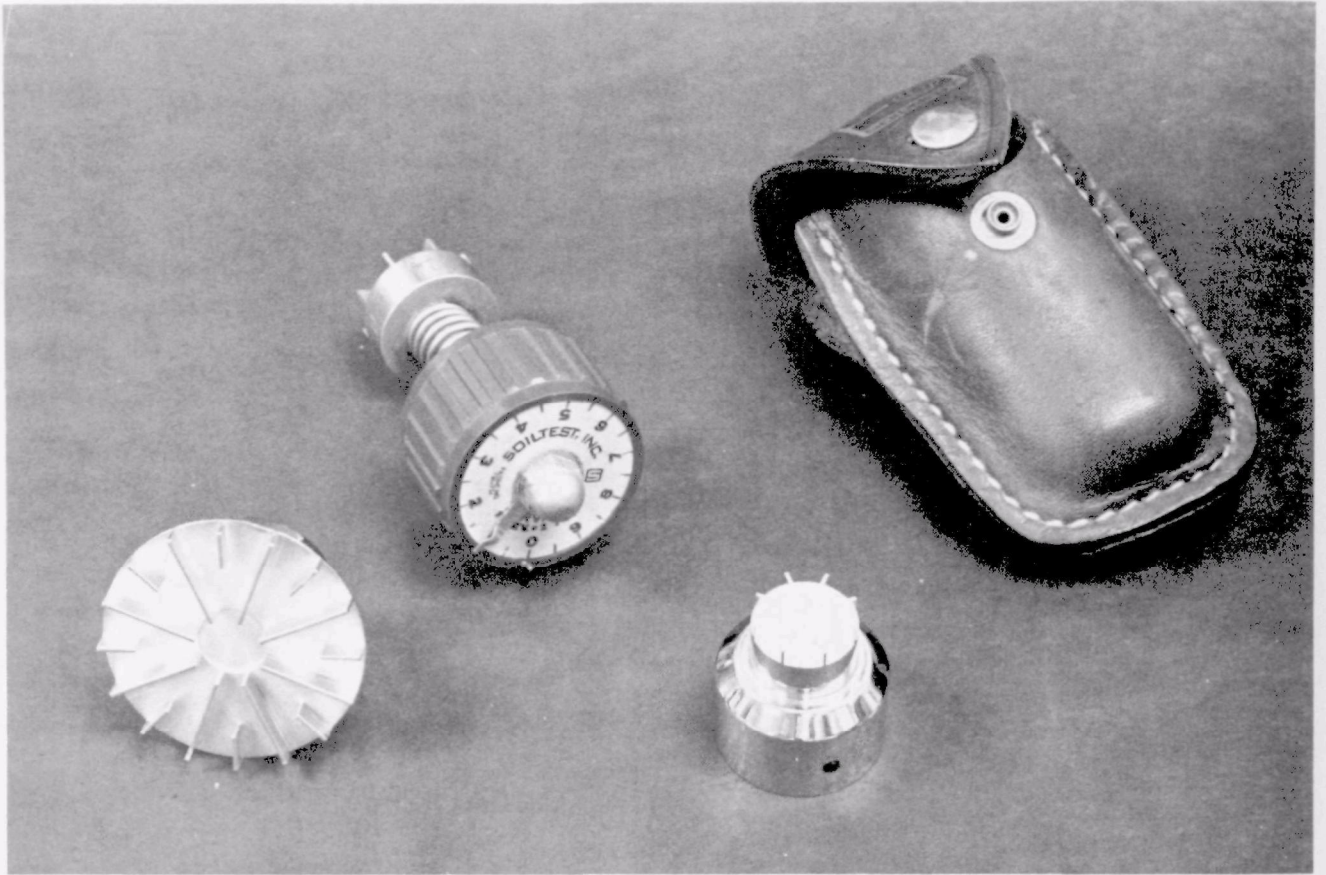
Figure 30. Torvane shear strength device (center), soft sediment adapter (left), and stiff sediment adapter (right).

Figure 31. Pocket penetrometer and soft sediment adapter.

Cost Analysis

Time required for each analysis (not including drying or cooling times): 15 min.

COST PER SAMPLE AT BATCH RATE $20
###

References

American Society for Testing and Materials, 1987. Annual book of standards: soil and rock, building stones and geotextiles, ASTM, Philadelphia, PA, vol. 04:08, 1189 pp.

Bowles, J. E., 1979. Physical and geotechnical properties of soils, McGraw-Hill, New York, NY, 478 pp.

Lee, H. J., 1985. State of tne art: laboratory determination of the strength of marine soils, in Chaney, R. C. and Demars, K. R., eds., Strength testing of marine sediments: laboratory and in situ measurements, American Society for Testing and Materials Special Technical Publication 883, Philadelphia, PA, pp. 181-250.

Noorany, I., 1985. Laboratory soil properties, in Rocker, Karl, Jr., ed., Handbook for marine geotechnical engineering, US Naval Civil Engineering Laboratory, Port Hueneme, CA, 19 pp.

CHAPTER 15

ONE-DIMENSIONAL CONSOLIDATION

Introduction

The constant-rate-of-strain consolidation (CRSC) test is performed to evaluate the laterally confined one-dimemsional stress-strain properties of a cylindrical wafer of sediment. Test results can be used to determine the stress history (maximum past stress) and the rate at which consolidation occurs. Typically, a test is performed in four parts: saturation, load, rebound and reload. Results from this test are often used to predict the amount and rate of settlement of a proposed engineering structure.

Procedure

Applicable ASTM standard: D4186-82, Standard test method for one-dimensional consolidation properties of soils using controlled-strain loading (ASTM 1987, pp. 709-715).

1. Flush the equipment lines with de-aired water to de-air the porous stones.

2. Place the test specimen into the CRSC system's confining ring, either by carefully trimming a sediment sample to the correct dimensions or by pushing a cutting ring into the sediment. Softer sediment typically requires the latter technique.

3. Trim the sample to the correct height with a wire saw and fill any irregularities in the sample with material from the trimmings. Obtain water content samples from the top, middle, and bottom trimmings.

4. Determine the weight and dimensions of the sample and record the data on a form similar to Figure 32.

5. Place the sample on the machine pedestal and assemble the confining apparatus, including filter papers and porous stones (Fig. 33).

6. Place the top cap on the sample. The top cap should be made of a strong, light-weight material. This is extremely important when testing very soft marine sediment.

7. Assemble the chamber and fili it with de-aired water.

CONSTANT RATE OF STRAIN CONSOLIDATION TEST

Test I.D./File Name:_____

Project Title:_____   Date/Start:_____ End:_____
(Cruise No.)
Core I.D.:_____   Tested By:_____

Subsectioned Interval (m):_____   Rate of Feed (mm/min):_____

Test Sample Interval (m):_____   Gearbox Lever (A-E):_____

System Number:_____   Cell Press. (kPa):_____

Readings:_____   Back Press. (kPa):_____

Raw Disc:_____   Reduced Disc:_____

PRE-CONSOLIDATION SPECIMEN DATA   WATER CONTENT FROM TRIMMINGS
                                              top   side   bottom
Diameter (mm)   _____   Container ID   ____   ____   ____

Height (mm)   _____   Wt. wet soil +
                                             container (g)   ____   ____   ____
Wt. cutting ring +   Wt. dry soil +
filter papers + sample (g)_____   container (g)   ____   ____   ____
Wt. cutting ring +   Wt. water (g)   ____   ____   ____
filter papers   (g)_____

                                           Wt. container (g)____   ____   ____

Wt. wet sample (g)   _____   Wt. dry soil (g) ____   ____   ____

SAMPLE DESCRIPTION AND COMMENTS   Water content (%)____   ____   ____

                                           w_c (%)   ____   ____   ____

                                           Average w_c (%)   _____

POST-CONSOLIDATION SPECIMEN DATA

Height (mm)   _____

Container I.D.   _____   Wt. wet sample + container (g)_____

Wt. dry sample + container (g)_____   Wt. dry sample + container (g)_____

Wt. container (g)   _____   Wt. water (g)   _____

Wt. Dry sample (g)   _____   Wt. dry sample (g)   _____

Wt. water (g)   _____

Water content (%)   _____   Water content (%)   _____

Pre-consol w_c (%)   _____   Post-consol w_c (%)   _____

Figure 32. Typical CRS consolidation test data form.
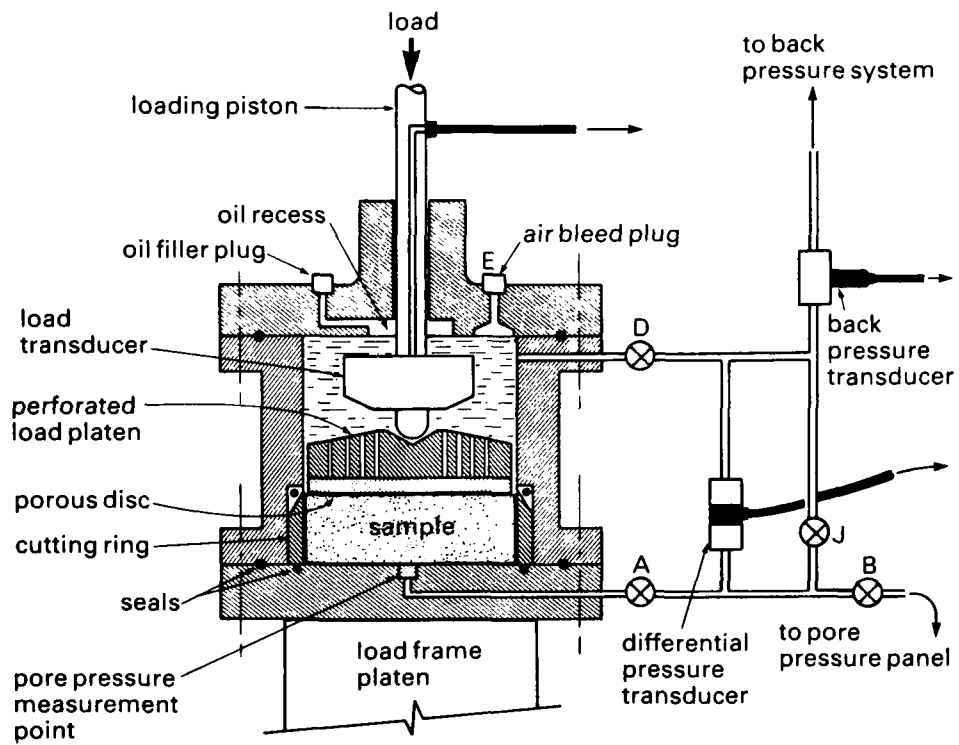
Figure 33. Typical constant-rate-of-strain consolidation (CRSC) sample and test chamber configuration (Head, 1986, p. 1208).

8. Connect the load, deformation, pore-pressure, and cell pressure (or differential transducer) measuring devices. Check that systems are operating correctly and that measurements are within bounds.

9. Make sure the sample does not swell. This is done either by limiting potential vertical deformation or by applying just enough seating stress to counteract the swelling tendencies of the sediment. It is extremely important to not overload the sample at this point.

10. Fully saturate the sediment interstitial pore spaces and equipment lines with water by dissolving any remaining bubble-phase gas. This is accomplished by elevating the cell pressure (often to 300 kPa) without allowing any pore fluid drainage. Determine a pseudo-B-coefficient if possible. The B-coefficient (change in pore pressure divided by change in chamber pressure) indicates complete saturation if the value is 1.00. Lower values typically represent partially saturated soils that may require higher stresses to ensure adequate saturation. An attempt should be made to reach full saturation, but, if this cannot be achieved, make sure that the sample is at least nearly saturated (B is less than 0.95) before continuing.

11. Let pore pressures within all systems and components equilibrate, often overnight.

12. Vertically strain the sample at a rate that will produce a change in pore pressure that is between 3 and 20 percent of the applied vertical stress at any time during the test. The strain rate may be adjusted during the test if it appears that the excess porewater pressure will not fall within those limits.

13. At discrete intervals, record load, deformation, cell pressure, and pore pressure response during the test.

14. If required, put a rebound curve into the test to determine unloading and recompression characteristics.

15. Continue to apply load until the capacity of the system is reached or until no further information is required.

16. Remove the sample from the testing device; determine dimensions, mass, and water content. Record information on a form similar to Figure 32.

17. Determine compression characteristics from the ASTM standard or other related articles dealing with this test (e.g., Lambe 1951, Lambe and Whitman 1969). The following plots should be generated for each CRSC test with the vertical effective stress (kPa, logarithm scale) as the abscissa: (1) void ratio, (2) excess pore pressure (kPa), (3) excess pore pressure divided by the total vertical stress (percent), (4) coefficient of consolidation (cm^2 per sec), and (5) coefficient of permeability (cm per sec). Test information can be summarized on a data sheet similar to Figure 34.

Comments

Although the CRS consolidation test is not often used for coarse-grained material, it is applicable to all fine-grained sediment. Very soft marine sediment, however, typically presents additional problems. When handling those samples, care must be exercised to avoid sediment deformation during the trimming process. Also, because normally consolidated and under-consolidated shallow-subbottom samples have typically experienced very low maximum past stresses, the sample must not be overloaded during the initial stages of the test. The piston bushings in the chamber must possess minimal friction or severe overestimations of the maximum past stress could result. To ensure the best possible test results, the sediment should be sampled, handled, transported, and stored in a manner that will minimally disturb the samples (see Chapter 2).

Note A less desirable method, using an oedometer apparatus, is sometimes used to determine consolidation properties of material. Because it utilizes an incremental loading schedule that requires complete dissipation of excess pore pressure between loadings, it is a very time-consuming test and often requires weeks to perform. The incremental loading test only gives one data point for each applied load (a load increment takes 12 to 24 h to complete), whereas the CRS consolidation test presents an almost continuous void ratio-stress curve. Within the above limitations, the incremental loading system is still adequate for testing most soils and it is, indeed, the more traditional approach. The ASTM standard for the incremental test is D2435-80, standard test method for one-dimensional consolidation properties of soils (ASTM 1987, pp. 388-394).

Quality Assurance

ASTM states that undisturbed soil samples from homogeneous soil deposits at the same location often exhibit significantly different consolidation properties. Because of sample variability, no method exists to evaluate the comparative precision of various consolidation tests on undisturbed samples.

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CONSTANT RATE OF STRAIN CONSOLIDATION TEST RESULTS

Test I.D./File Name:_____

Project/Cruise:_____ Date Core Obtained:_____

Location of Core:_____ Lat.:_____ Long.:_____

Core Retrieval:_____ Shape & Dimensions:_____

Method of Shipping & Handling:_____

Storage:_____ Temperature:_____

Problems in Handling/Storage:_____

Boring/Core ID:_____

Extruded Sample Increment (m):_____ Tested Sample Increment (m):_____

Type of Material:_____

Problems/Comments of Test:_____

Validity/Discrepancies of Test:_____

Frame:_____ Load Cell:_____ u Trans.:_____ LVDT:_____

Test Performed By:_____ Date of Consol.:_____

Data Reduction By:_____ Date:_____

Checked By:_____ Date:_____

Raw Disc:_____ Reduced Disc:_____

Saturation Pressure (kPa):_____

Strain Rate (mm/min):_____ Time for Consol:____/____/_____
                                          (day/hour/min):
B Coefficients; Initial:_____ Final:_____

Bulk Density Before Consolidation (kNm^3):_____ Area (cm^2):_____

Heights (cm); Initial:_____ Final:_____

Water Content (%); Trimgs:_____ Calc. Init.:_____ Final:_____

Ave. w Above Test Sample (%):_____; G_s:_____; Meas:_____; Assumed_____

Ave. G_s Above Test Sample:_____; Meas:_____; Assumed:_____

Average Effective Unit Wt (kN/m^3):_____

σ'_{vo} (kPa):_____; σ'_{vm} (kPa):_____; Casagrande:_____; Other:_____

σ'_e (kPa):_____; OCR:_____

Figure 34. Constant-rate-of-strain consolidation test summary form.

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C_c (lab); max:_____; ave:_____; min:_____; C_c (field):_____

C_r (lab):_____

c_v (cm^2/sec) @ σ'_{vo}:_____; @ σ'_{vm}:_____; ave. virgin:_____

k (cm/sec) @ σ'_{vo}:_____: @ σ'_{vm}:_____; ave. virgin:_____

$$I_D = \frac{e1 - e2}{e1 - e3} = \underline{\hspace{2cm}} =$$

e_o:_____;   0.42 e_o:_____

A classification based on disturbance index might be as follows:

Disturbance Index, I_D	Degree of Disturbance
.15	Very little disturbance ("undisturbed")
.15-.30	Small amount of disturbance
.30-.50	Moderate disturbance
.50-.70	Much disturbance
.70	Extreme disturbance (remolded)
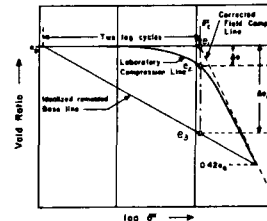
Curve Type: normal_____, sensitive_____, remolded_____, continuous curve_____

rebound changes C_c slope: no_____, yes_____

Test Suite Results: averaged_____, weighted_____

σ'_{vo} (kPa):_____ σ'_{vm} (kPa):_____

σ'_e (kPa):_____   OCR:_____

C_c (lab): max:_____, ave:_____, min:_____; C_c (field):_____

C_r (lab):_____

c_v (cm^2/sec) @ σ'_{vo}:_____, @ σ'_{vm}:_____, ave. virgin:_____

k (cm/sec) @ σ'_{vo}:_____, @ σ'_{vm}:_____, ave. virgin:_____

I_D:_____

Comments/Notes:_____

_____

_____

_____

_____

_____

Figure 34. (cont). Constant-rate-of-strain consolidation test summary form.

A suitable test material and method of sample preparation have not been developed for determining laboratory variances due to the difficulty in producing identical cohesive soil samples. Therefore, no estimates of precision for this test method are available.

Cost Analysis

Time required for each consolidation test (not including drying or cooling times): 2 to 4 days

COST PER CONSOLIDATION TEST $400

###

References

American Society for Testing and Materials, 1987. Annual book of standards, soil and rock, building stones and geotextile, ASTM, Philadelphia, PA, vol. 04:08, 1189 pp.

Head, K. H., 1986. Manual of soil laboratory testing, volume 1: soil classification and compaction tests, Pentech Press, London, 339 pp.

Lambe, T. W., 1951. Soil testing for engineers, John Wiley, New York, NY, 165 pp.

Lambe, T. W. and Whitman, R. V., 1969. Soil mechanics, John Wiley, New York, NY, 553 pp.

CHAPTER 16

STATIC CONSOLIDATED-UNDRAINED TRIAXIAL COMPRESSIVE STRENGTH

Introduction

The triaxial test measures the drained and undrained stress-strain properties of soil. A right-circular cylinder of sediment is enclosed in a watertight membrane within a fluid-filled test chamber. After saturation of entrapped bubble-phase air into the pore water is completed, radial and vertical stresses on the sample are elevated and consolidation is allowed by permitting drainage. After consolidation is finished, the sample is vertically loaded at a constant strain rate until failure (typically 15 percent strain) is reached. This predetermined strain level will, in most cases, allow the sample to reach its peak strength. While sample compression is progressing, either the operator or an automatic data acquisition system is recording axial load, axial deformation, pore pressure, and cell pressure.

Although three main types of triaxial tests are performed [unconsolidated-undrained (UU), consolidated-drained (CD), and consolidated-undrained (CU)], the test method discussed here pertains specifically to the CU test. However, with only slight modifications in the testing procedure, the other two types of tests can be run.

The shear strength of sediment in triaxial compression depends on the stresses applied, the time allowed for consolidation, the strain rate, and the stress history of the soil. In this test, strength is measured under undrained conditions, and the test is applicable to field conditions where soils that have fully consolidated under one set of stresses are subjected to a rapid stress change without time for drainage to occur. Data from the test can be used to determine soil characteristics in terms of total or effective stresses.
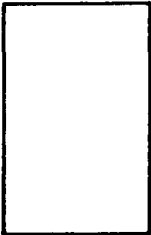
Procedure

ASTM does not have a standard for the consolidated-undrained test, although one is presently in review. However, it does give a test standard for the unconsolidated-undrained test (D2850-82, standard test method for unconsolidated, undrained compressive strength of cohesive soils in triaxial compression (ASTM 1987, pp. 451-456).

1. Apply silicone grease to the triaxial-chamber bottom pedestal and to the sample's top cap.

2. Flush all system lines with de-aired water. Some investigators use salt water in the pore pressure lines; however, that fluid has a severe corrosive effect on most metal fittings. De-air the porous stones by boiling.

3. Trim the sediment sample to the appropriate dimensions: its height should be approximately twice its diameter. For most sediment, a standard soil lathe can be used for trimming. However, some extremely soft marine sediments will deform under their own weight if left standing. For those sediments, a miniature thin-walled piston sampler can be used to obtain a relatively undisturbed sample (Winters 1987). In operation, the piston is held fixed at the sediment surface while the thin-walled tube, having an inside diameter equal to the outside diameter of the test sample, is pushed into the sediment. Although this sampling technique disturbs the sediment somewhat, the procedure does allow otherwise unsuitable sediment to be tested. Record applicable information on a data form similar to Figure 35.

4. Quickly place the sample on the triaxial machine pedestal, making sure that the top and bottom porous stones and filter papers are in the correct position.

5. Place the top cap, made of a strong, light-weight material, on the sediment.

6. Place radial filter paper drains on the sample.

7. Place a thin membrane over the sample and seal both the bottom pedestal and top cap with two 0-rings.

8. Assemble the chamber and fill it with de-aired water (Fig. 36).

9. Connect all measuring devices (load cell, strain gauge, pore- and cell-pressure measuring devices or differential transducer) to the chamber after ensuring that they are operating correctly.

10. Slowly saturate the sample by simultaneously or alternately increasing the cell pressure and back pressure in less than 50-kPa increments. Do not saturate in increments greater than the final consolidation stress. Final back pressure should be at least 300 kPa.

11. After saturation is complete, usually overnight, as indicated by a B coefficient (change in pore pressure divided by the change in cell pressure) greater than 0.95, allow all stresses to equilibrate.

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TRIAXIAL DATA SHEET

Test ID/   Test ID/
Consol. File Name:_____   Shear File Name:_____
Project Title:_____   Date/Start:_____ End:_____
(Cruise No.)
Core ID:_____   Tested By:_____
Subsectioned Interval (m):_____   Rate of Feed (mm/min):_____
Test Sample Interval (m):_____   Gearbox Lever (A-E):_____
System Number:_____   Cell Press. (kPa):_____
Raw Disc:_____   Back Press. (kPa):_____
Reduced Disc:_____   Consol. Stress (kPa):_____
Consol. Rdgs.:_____ - _____   Shear Rdgs.:_____ - _____

Filter papers:_____
Membrane:_____
"B" value from printout: _____   INIT RDGS   SHEARED SAMPLE
Final Dvol rdg. (cc):_____   PP kPa:_____
Initial Dvol rdg. (cc):_____   DL mm:_____
Total water expelled (cc):_____   AX kN:_____
Trimmed Diameter (mm):_____   CP kPa:_____
Trimmed Ht. (mm):_____
Piston Factor (mm):_____ w_c:_____
Piston Ht. (mm):_____ G_s:_____
Init. Ht. (PH-PF) (mm):_____
Piston Ht. (mm):_____   POST SHEAR
Calc. Post-Consol Ht. (mm):_____   CP = _____
Piston Ht. (mm):_____   PP = _____
Calc. Post-Shear Ht. (mm):_____   C-P = _____
Post-Consol Ht. (LVDT) (mm):_____
Meas. Post-Shear Ht. (mm):_____

    WATER CONTENT FROM TRIMMINGS   PRE-SHEAR SPECIMEN DATA
                    Top Side Bottom
Container ID   ____ ____ ____   Wt. 2 f.p. + wet sample (g)   _____
Wt. wet soil +
 container (g)   ____ ____ ____   Wt. 2 f. papers (g)   _____
Wt. dry soil +   Wt. wet sample (g)   _____
 container (g)   ____ ____ ____   Wt. dry sample (below) (g)   _____
Wt. water (g)   ____ ____ ____   Wt. water (g)   _____
Wt. container (g)   ____ ____ ____   Water content (%)   _____
Wt. dry soil (g)   ____ ____ ____ w_c (%)   _____
Water content (g)   ____ ____ ____
w_c salt corrected(%) ____ ____ ____   POST-SHEAR SPECIMEN DATA
Average w_c (%)   _____
SAMPLE DESCRIPTION   Container ID   _____
                                              Wt. wet sample +
                                              membrane + cont. (g)   _____
                                              Wt. dry sample + cont. (g)   _____
                                              Wt. membrane (g)   _____
                                              Wt. container (g)   _____
                                              Wt. wet sample (g)   _____
                                              Wt. dry sample (g)   _____
                                              Wt. water (g)   _____
                                              Water content (%)   _____
                                              w_c (%)   _____

─────────────────── COMMENTS AND OBSERVATIONS ───────────────────

Figure 35. Typical triaxial test data form.

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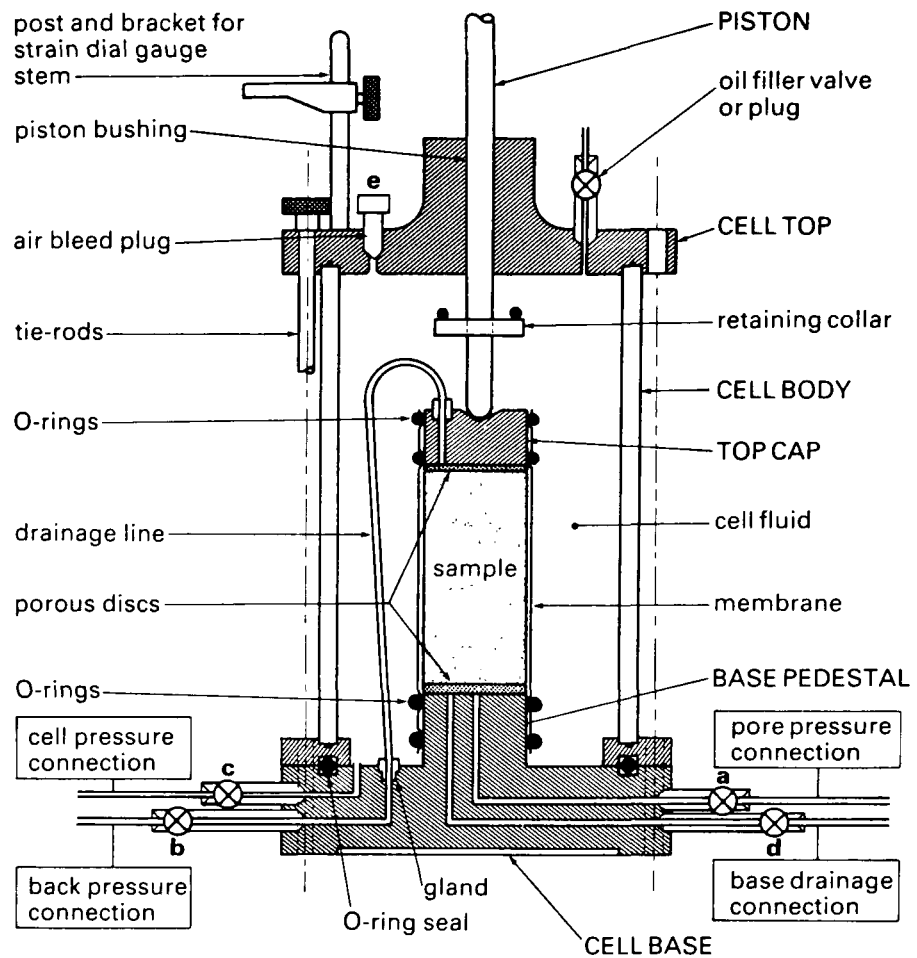
Figure 36. Typical components of a triaxial test device (Head, 1986, p. 801).

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12. Consolidate the sample to the required stress by elevating the cell pressure above the back pressure and permitting drainage. Sometimes, especially if large consolidation stresses are to be applied to very soft sediment, the final consolidation state is reached by alternately increasing the cell pressure and allowing drainage between increments. Plot the volume change of the sample according to the log-time or square-root-time method (Bishop and Henkel 1962, and Department of the Army 1980). If the log-time method is used, allow consolidation to continue for at least one log cycle of time (or overnight) after primary consolidation has ceased. If the square-root-time method is used, consolidation should continue for at least 2 h after primary consolidation has ceased.

13. Close the drainage valve and shear the sample at a constant rate such that pore-pressure equalization occurs throughout the sample. For fine-grained sediment, an appropriate strain rate typically will cause 15 percent strain to occur after several hours. If a test is performed at too fast a rate, severe pore-pressure measurement inaccuracies could result.

14. Measure and record load, deformation, and pore- and cell-pressure (or differential transducer) readings throughout the test.

15. Continue loading until 15 percent axial strain occurs.

16. Remove the sample from the chamber. Record the dimensions and mass on a data form similar to Figure 35.

17. Perform required calculations and plot data as specified (Bishop and Henkel 1962, Head 1986). As a minimum, the following plots should be produced: (1) volume change during consolidation (cc) versus the square root or logarithm of time (min); (2) q (o_1 minus o_3) divided by 2; (3) q (kPa) versus strain (percent); and (4) change in pore pressure (kPa) versus strain (percent). The results can be summarized on a form similar to Figure 37.

Comments

The consolidated-undrained triaxial compressive strength with pore pressure measurement test is a valuable tool. In addition to determining static strength characteristics that could be used for total stress analyses such as waste package seabed penetration, the test can also be used to measure drained parameters that are useful for analyzing slower in situ shear mechanisms where sufficient time is available for complete pore-pressure dissipation.

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TRIAXIAL SAMPLE AND TEST DATA

Test No.:_____

Project/Cruise:_____   Date Core Obtained:_____

Location of Core:_____   Lat.:_____ Long.:_____

Core Retrieval:_____   Shape & Dimensions:_____

Method of Shipping & Handling:_____

Storage:_____   Temperature:_____

Problems in Handling/Storage:_____

Boring/Core ID:_____

Extruded Sample Increment (cm):_____ Tested Sample Increment (cm):_____

Type of Material:_____

Type of Test:_____

Problems/Comments of Test:_____

Validity/Discrepancies of Test:_____

Frame:_____ Load Cell:_____ u Trans.:_____ LVDT:_____ DVOL:_____

Test Performed By:_____   Date of Shearing:_____

Data Reduction By:_____   Date:_____

Checked By:_____   Date:_____

Raw Disc:_____   Reduced Disc:_____

Type of Consolidation:_____

Maximum Past Vertical Stress (kPa):_____ Determined By:_____

Back Pressure(kPa):   ____, ____, ____, ____, ____, ____, ____

Radial Consolidation Pressure (kPa): ____, ____, ____, ____, ____, ____, ____

Vertical Consolidation Pressure (kPa):____, ____, ____, ____, ____, ____, ____

Induced OCR:_____ OCR Based On:_____

Strain Rate (mm/min):_____ Time of Shearing (min):_____

Type of Membrane:_____ Thickness (cm):_____

Type & Material of Drain(s):_____ Thickness (cm):_____

Figure 37. Consolidated-undrained triaxial compressive strength test summary
         form.

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Height/Diameter; Trimmed:_____ Tested:_____

Membrane Correction Applied:_____ Filter Drain Correction Applied:_____

Bulk Density Before Consolidation (kNm^3):_____

Heights (cm); Initial:_____ Consolidation:_____ Final:_____

Water Content (%); Initial:_____ Consolidation:_____ Final:_____

Volume (cm^3); Initial:_____ After Consolidation:_____

Area (cm^2); Inital:_____; Consol. Area (cm^2)=A_c=$\dfrac{Consol.\ volume}{Consol.\ Height}$ _____

B Coefficients; Before Consolidation:_____

          After Consolidation:_____, _____

          Before Shearing:_____

At Failure; q (kPa):_____ p' (kPa):_____

          A Coefficient:_____

          Change in Pore Water Pressure (kPa):_____

          Axial Strain (%):_____

          Type of Failure:_____

          ϕ' (maximum) (degrees):_____ Su/p' = c/p':_____

          ϕ' (at maximum q) (degrees):_____

          ϕ' (at peak-max. obl.) (organics only) (degrees):_____

Comments/Notes:_____

_____

_____

_____

_____

_____

Figure 37. (cont). Consolidated-undrained triaxial compressive strength test summary form.

Almost all deep-sea sediments can be tested using the procedures described above. However, particles that are greater than 1/6 the diameter of the test sample must not be present prior to testing. To insure that the best possible test results are obtained, the sediment should be sampled, handled, transported, and stored in a manner that will minimally disturb the samples (see Chapter 2).

Testing soft sediment presents special problems. Extreme care must be exercised in the handling and trimming of the samples. Friction in the top-cell piston bushing should be minimal or severe strength overestimations can result. Thin membranes, e.g. prophylactics, should be used so that inordinate amounts of measured load won't be due to membrane stiffness.

Opinions vary on how to obtain strength measurements in certain circumstances. Some investigators would suggest consolidating to the in situ overburden stress; some wouldn't consolidate the sample at all; and others would first consolidate to stresses much higher than the in situ values, then, knowing the stress history, would back calculate what the undrained shear strength could be. A combination of all three test types is possible. More sophisticated tests, e.g. anisotropically consolidated triaxial strength tests, can also be performed. Lee (1985) presents a summary of current methodologies used for performing triaxial testing on marine sediment.

When evaluating the strength characteristics of marine sediments, a laboratory that has had previous experience in determining and interpreting offshore strength characteristics should be consulted.

Quality Assurance

Methods for determining accuracy and precision have not been formulated for the CU triaxial test by ASTM. Lee and Clausner (1979) state that even when using special techniques to minimize disturbance, the best accuracy attainable is +/- 20 percent. Typically, accuracy is much worse.

Cost Analysis

Time required for each triaxial test (not including drying and cooling times): 2 to 4 days

COST PER TRIAXIAL TEST $400

###

References

American Society for Testing and Materials, 1987. Annual book of standards, soil and rock, building stones and geotextiles, ASTM, Philadelphia, PA, vol. 04:08, 1189 pp.

Bishop, A. W. and Henkel, D. J., 1962. The measurement of soil properties in the triaxial test: Edward Arnold, London, 227 pp.

Head, K.H., 1986. Manual of soil laboratory testing, volume 3: effective stress tests, John Wiley, New York, NY, pp. 743-1238.

Lee, H. J., 1985. State of the art: laboratory determination of the strength of marine soils, in Chaney, R. C., and Demars, K. R., eds., Strength testing of marine sediments: laboratory and in situ measurements, American Society for Testing and Materials Special Technical Publication 883, Philadelphia, PA, pp. 181-250.

Lee, H. J. and Clausner, J. E., 1979. Seafloor soil sampling and geotechnical parameter determination handbook, US Naval Civil Engineering Laboratory Technical Report R873, Port Hueneme, CA, 128 pp.

US Department of the Army, 1980. Laboratory soils testing in Engineer Manual EM 1110-2-1906, Washington, DC, 388 pp.

Winters, W.J., 1987. Guidelines for handling, storing, and preparing soft marine sediments for geotechnical testing, US Geological Survey Open-File Report 87-278, 11 pp.

APPENDIX A

Preparation of Randomly Oriented Mounts

For X-ray Diffraction

154

Preparation Of Randomly Oriented Mounts
For X-ray Diffraction

1. Materials Required:
   plastic tape
   weighing paper
   pestle and mortar
   stiff brush
   .063 mm sieve
   spatula
   pencil
   sample holder
   2 pieces of glass
     slide cut to cover
     the sample holder
     opening
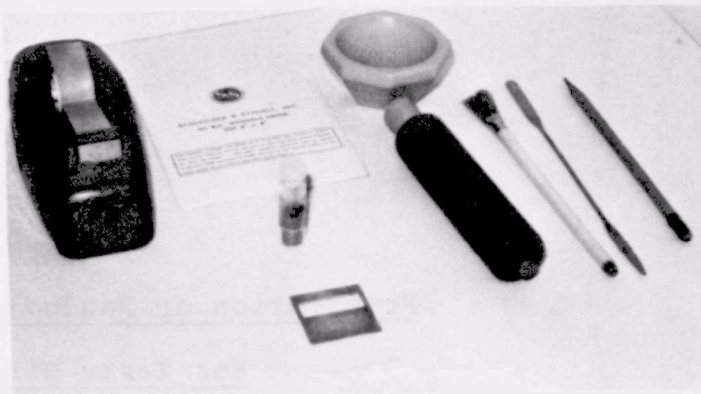
2. Tape one cover glass
   over the opening of the
   sample holder. Leave a tab
   for later removal. Fold
   the tape against itself
   so that it will not stick
   to other objects. Place the
   glass slide down on a piece
   of weighing paper.

3. Grind the sample throughly
   so that all of it can be
   brushed easily through a
   230 mesh (:063 mm) sieve.
   The particles must be much
   finer than .063 mm to avoid
   size fractionation of the
   minerals. The sieve is used
   only to achieve even
   distribution.
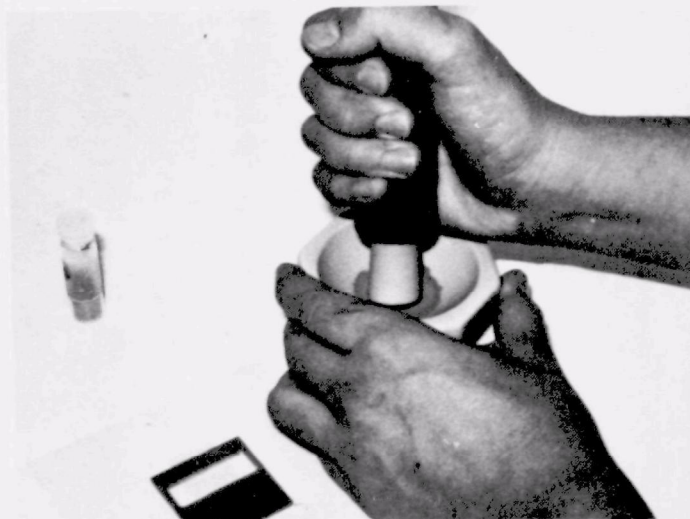
4. (optional) Place a
   second holder over the
   first as a mask. This
   enables the buildup of
   a thick enough layer
   for later packing down,
   while maintaining a
   clean metal surface on
   the first holder.

5. Place the sieve over the
   sample holder and brush
   the sample from the mortar.
   (Note: the sample may
   become contaminated with
   trace amounts of elements
   from the sieve and utensils.
   These will not be detectable
   by X-ray diffraction but may
   affect the results of
   emmision spectroscopy. Do
   not plan to reuse this cut
   for sensitive chemical
   analyses.

6. Use the spatula to loosen the
   sample that has stuck to the
   mortar and brush the material
   into the sieve.

7. Brush the sample through the sieve into the cavity of the sample holder. The purpose of the brushing is to obtain even distribution and minimize perferred orientation of the particles.

8. Remove the sieve and mask.
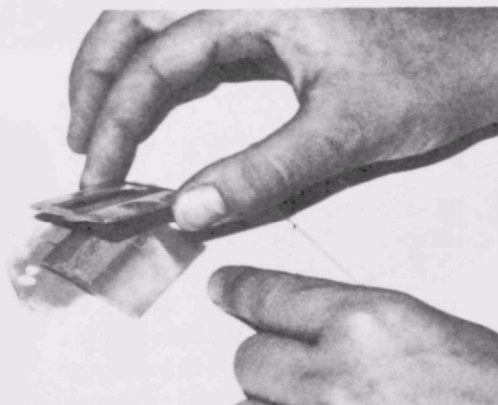
9. Place the sample holder on a clean piece of weighing paper, tap the powder remaining on the mask onto the first weighing paper and replace the mask over the sample holder.

10. Pour the excess powder on the first weighing paper into the sample holder. Distribute the powder evenly.

11. Use a glass slide to pack the sample into the holder firmly enough so that it will not fall out, deform, or slide, but not so firmly that perferred orientation will be produced on the opposite surface (that will later become the top surface).

12. Add sample from the vial as a filler if necessary to creat a firm pack. This part of the sample need not be as firmly ground, as it will become the bottom surface and will not be exposed to the X-ray beam.

13. Pack as in step 11 above, then tape a glass cover on the surface of the holder or use a metal backing clip (not shown). The tape will not stick if powder remains on the metal surface. First hold the cover glass in place and wipe the metal surface with your finger. Fold a little tab of the tape as before.

14. Turn the sample holder over so that the bottom side faces up. Carefully lift the first tab of tape and remove the cover slide. This will be the surface exposed to X-rays and should be smooth, uniform, and flush with the metal surface. If not remake the mount.

15. Label the sample holder with a pencil.
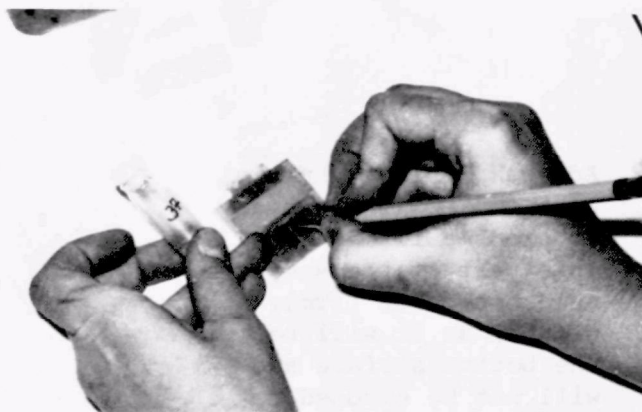
APPENDIX B

Separation of Clay Fraction

APPENDIX B
Separation Of Clay Fraction

1. Materials required:
   50 ml centrifuge tubes
   centrifuge tube caps
   250 ml beakers
   evaporating dishes
   test tube rack
   sodium metaphosphate
   spatula
   marking pencil
   lab tissues
   ultra sonic probe
   Vortex mixer
   stop watch
   thermometer

2. Label centrifuge tubes
   with the marking pencil.

3. Label 250 ml beakers
   with the marking pencil.

4. Label evaporating dishes
   with the marking pencil.
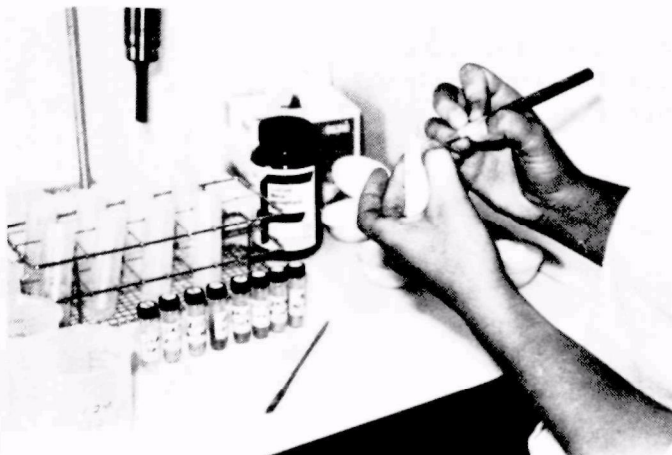
5. Pour enough sample to
   fill the rounded part
   of the bottom of the
   centrifuge tubes.
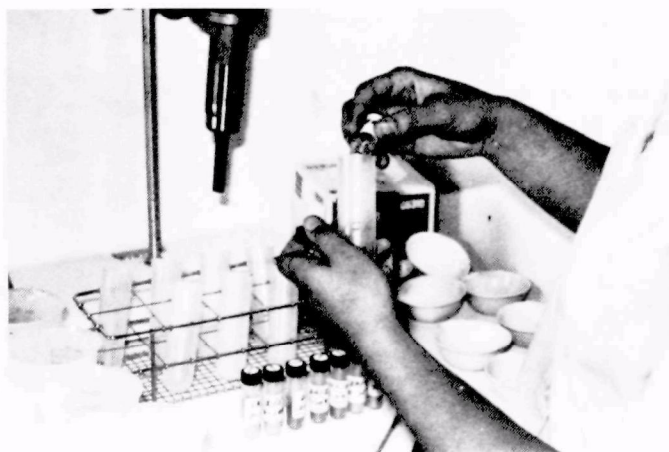
6. Add an amount of sodium
   metaphosphate to cover
   the end of a narrow
   spatula as shown.
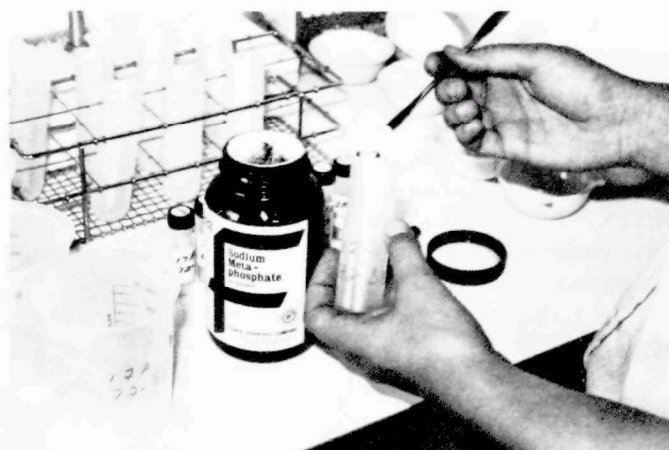
7. Add distilled water to fill the tube slightly more than half full.
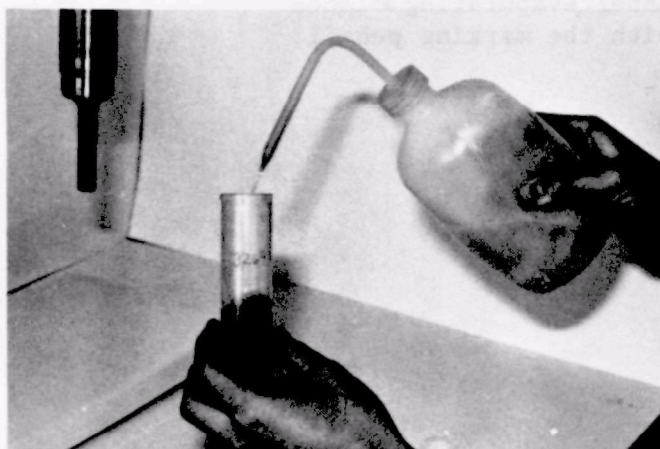
8. Place cap on the centrifuge tube.

9. Place tube on the Vortex mixer, press down and tip tube to the side to achieve vortex. Be carefull that your fingers do not smear the labeling on the tube. Mix until sediment in bottom of tube is aa in suspension.

10a. Rinse and wipe off
     tip of ultrasonic
     probe.
  b. Turn on ultrasonic
     probe power supply.
  c. Adjust for maximum
     power.

11. Disperse sample for
    15-20 seconds with
    ultrasonic probe.

12. Add distilled water
    to fill tube to with-
    in 1 cm of the top of
    the tube, place cap
    on tube and mix the
    contents using the
    Vortex mixer.
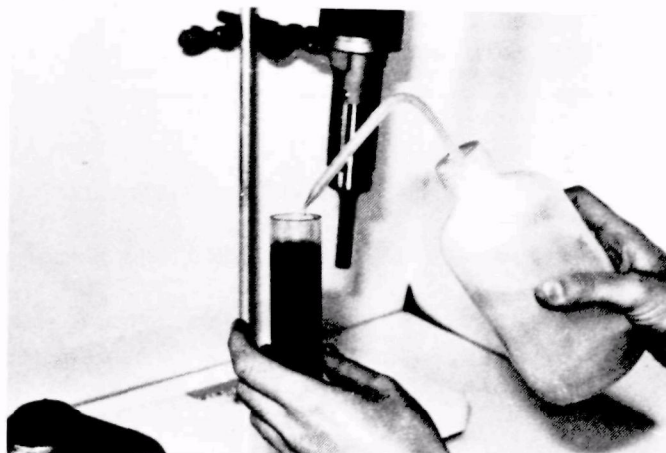
13. Place tubes in centrifuge. Be sure centrifuge is balanced by having the opposite tubes filled equally. 2, 4, 6, or 8 tubes may be used. Close cover.
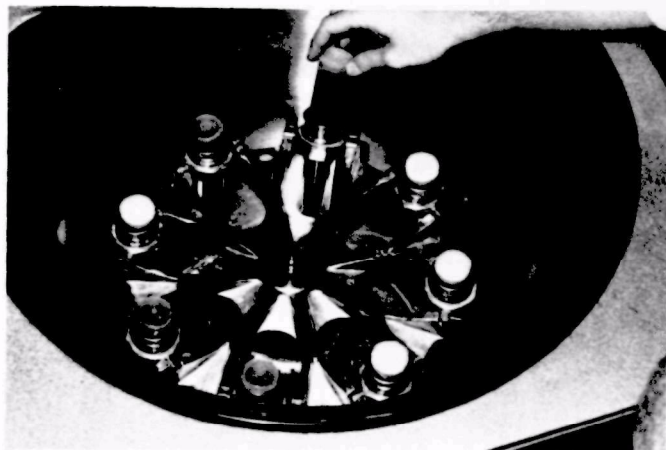
14. Check water temperature and find centrifuging time in minutes and seconds (Table B-1).
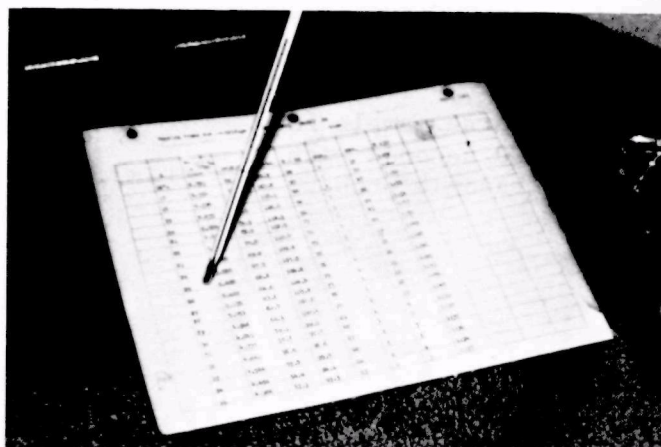
15. Turn power switch to "not timed". Turn speed controller first to zero and then to 40.

t	$b = \dfrac{\bar{p} - \bar{p}_c}{} \times 1000$	c=12.22b	T=c+40	T - td	min.	sec.	T +30
16°c	6.723	82.2	122.2	92	1	32	1:62
17	6.554	80.2	120.2	90	1	30	1:60
18	6.396	78.1	118.1	88	1	28	1:50
19	6.235	76.0	116.0	86	1	26	1:56
20	6.084	74.3	114.3	84	1	24	1:54
21	5.938	72.5	112.5	83	1	23	1:53
22	5.800	70.8	110.8	81	1	21	1:51
23	5.666	69.2	109.2	79	1	19	1:49
24	5.529	67.5	107.5	78	1	18	1:48
25	5.408	66.2	106.2	76	1	16	1:46
26	5.287	64.6	104.6	75	1	15	1:45
27	5.172	63.2	103.2	73	1	13	1:43
28	5.054	61.8	101.8	72	1	12	1:42
29	4.946	60.4	100.4	70	1	10	1:40
30	4.843	59.1	99.1	69	1	9	1:39
31	4.737	57.7	97.7	68	1	8	1:38
32	4.640	56.6	96.6	67	1	7	1:37
33	4.544	55.5	95.5	66	1	6	1:36
34	4.450	54.4	94.4	64	1	4	1:34
35	4.366	53.3	93.3	63	1	3	1:33

Table B-1. Table constructed from the formula given below and in Hathaway (1956) to show the relationship between the temperature of the sediment suspension and the centrifuging time necessary to separate the silt and clay fractions at 2 micrometers. T+30 is the total centrifuging time

counting acceleration and deceleration. T-td is the time at which decelera-
tion is started. This table assumes a ratio of starting radius of the
particle from the axis of the centrifuge to the ending radius (bottom of the
centrifuge tube) of 1.787, a centrifuge speed after 30 seconds of accelera-
tion of 1400 rpm, a deceleration time of 30 seconds, and a particle density
of 2.65.

The formula may be represented by the equation

$$T = \frac{\eta \log 10 \frac{R_2}{R_1}}{3.81 r^2 N^2 (p - p_o)} + \frac{2(ta + td)}{3}$$

where:
- T total time in seconds
- ta time of acceleration
- td time of deceleration
- η viscosity in poises
- R_1 initial distance from the axis of rotation
- R_2 final distance from the axis of rotation
- r radius of the particle in centimeters
- N angular velocity in revolutions/second
- p density of the particle in grams/cm^3
- p_o density of the medium in grams/cm^3

For ta and td the acceleration and deceleration are assumed to be
constant.

16. When needle of the tachometer starts to move (tap it to make sure it starts) start stop watch and move speed controller to 52.

17. When the needle reaches 700 rpm turn speed controller to 65.

18. When the needle reaches 1400 rpm (this should take about 30 seconds from the start of the stop watch) move speed controller back to 52. Adjust speed if necessary to keep needle on 1400 rpm.

19. When the stop watch reads the time determined from the table, turn the power switch off and return speed controller to zero.

20. Allow machine to coast down to 1000 rpm. Then push brake button momentarily several times to maintain a constant rate of deceleration.

21. Speed should read near zero by the time the stop watch reads T+30 seconds.

22. Remove tubes from the centrifuge, pry off caps, and pour super-natant liquid into the appropriate beakers. Be careful that the sediment in the bottom of the tube is not poured off. Repeat steps 7 through 22 until the supernatant liquid is clear (about 4 or 5 times).

Silt Fraction Preparation

1. Use squeeze bottle with distilled water to wash residue in bottom of centrifuge tube into evaporating dish.

2. Place evaporating dish into circulating oven at 60-70°C.
3. Remove when dry and scrape silt into a sample vial.
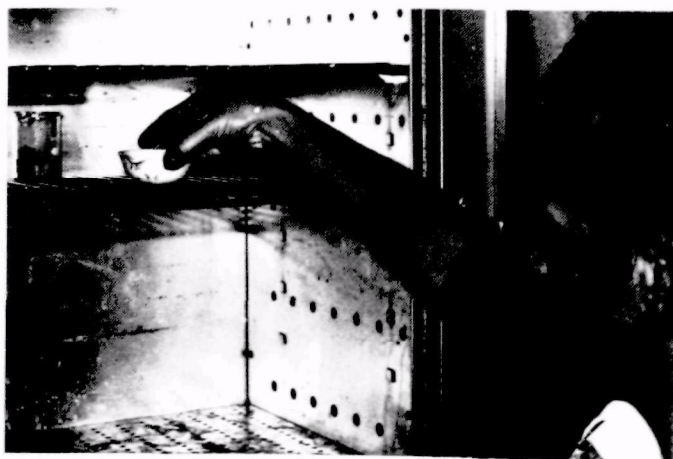
APPENDIX C

Silver Filter Preparation

APPENDIX C
Silver Filter Preparation

This method shows the use of one whole silver filter per sample. A more economical practice would be to cut each filter in half, thereby getting two samples X-rayed per filter. This is possible because only an area 2 cm by 1 cm is actually subjected to the X-ray beam and a mask may be constructed so that only this area is exposed during filtration. This technique has the added advantage in that a smaller sample would be concentrated into a smaller area and thus give better diffraction maxima.

1. New silver filters should be soaked in alcohol overnight, then rinsed with alcohol on the filtering apparatus. Label the filter around the edge with a pencil; write lightly, the filters are delicate.

2. Center filter on vacuum filter apparatus.

3. Place filter funnel on top of the filter and clamp it down.

4. Pour a small amount of the sample suspension into the filter funnel (enough to cover the filter). Repeat after the water is pulled through the filter.

5. Remove clamp and filter funnel and pry up an edge of the filter with a pointed spatula or razor blade.

6. Lift filter with filter forceps and place it in a plastic capsule to dry and store till X-ray analysis.

APPENDIX D

Ethylene Glycol Vapor Treatment

1. Pour ethylene glycol
   to about 1 cm depth
   in base of desiccator.

2. Place silver filter
   with oriented clay
   aggregate on shelf
   of desiccator.
   Additional shelves
   may be stacked if
   necessary.

3. Place desiccator in
   oven at $60^{\circ}-70^{\circ}$C for
   about four hours.
   Longer times will not
   hurt the samples. Do
   not remove filters
   until they are run on
   the X-ray diffractometer.

APPENDIX E

Heat Treatment

1. Set temperature
   control to 400°C.

2. Place filter in
   oven using tongs.
   Leave sample in
   oven for 1/2 hour.

3. Remove filter by
   pulling it forward
   with a wire hook
   until the front of
   the filter can be
   grasped by the tongs.

4. X-ray the sample and
   repeat the procedure
   at 550°C.

APPENDIX F

Flow Charts For Identifying Clay Minerals

With Various 001 Diffraction Maxima

Sample

Disaggregation, fractionation

Clay <2μ   Silt 2-62μ   Sand >62μ

2-20μ   20-62μ

X-rays of oriented aggregates

X-rays of randomly oriented powders

Air dried | Treated with ethylene glycol at least ½ hr, 4 hrs. by vapor pressure method | Heated to 400°C at least ½ hr | Heated to 550°C at least ½ hr | Electron micrograph if required

6   7   8   9   10

1   2   3   4   5

if required

Non-clay minerals determined by comparison of patterns 6, 7, 8, 9 and 10 with standard patterns

~29Å → Expands to 31-32Å with rational sequence of higher orders → May disappear or give 24Å spacing → Increase in intensity of 24Å spacing → Regularly interstratified chlorite-montmorillonite or chlorite-vermiculite "corrensite"   15/

Expands but gives irrational sequence Peaks may be broad → May give irrational sequence → May give irrational sequence--may show increase in intensity of 12-14Å peak → Randomly interstratified chlorite-montmorillonite   14/

~14Å → No change → No change → Increase in intensity → 060 near 1.54Å → Chlorite   5/

060 near 1.50Å → Dioctahedral chlorite   7/

No change or slight increase → Collapses to ~10Å → No change or slight additional collapse → 060 near 1.54Å → Vermiculite   17/

Slight collapse ~12Å → Additional collapse ~11Å → 060 near 1.50Å → Dioctahedral vermiculite   12/

Expands to 17Å → Collapses to ~10Å → No change or slight additional collapse → 060 near 1.50Å → Montmorillonite   16/

Collapses to ~10Å with very weak 5Å peak → No change or slight additional collapse → 060 near 1.52Å → Nontronite

060 near 1.54Å → Trioctahedral montmorillonite or vermiculite   16/ 17/ 14/

Check with glycerol treatment
Montmorillonite gives 17.7Å
Vermiculite gives 14-15Å

APPENDIX F

Flow chart for the identification of clay minerals with 001 diffraction maxima at 29 or 14 angstroms on the air dried pattern. Chart shows the effects of ethylene glycol and heat treatments on the location of these peaks.

Sample

Disaggregation, fractionation

Clay <2µ   Silt 2-62µ   Sand >62µ

2-20µ   20-62µ

X-rays of oriented aggregates

X-rays of randomly oriented powders

Air dried | Treated with ethylene glycol at least ½ hr, 4 hrs. by vapor pressure method | Heated to 400°C at least ½ hr | Heated to 550°C at least ½ hr | Electron micrograph if required

6   7   8   9   10

if required

Non-clay minerals determined by comparison of patterns 6, 7, 8, 9 and 10 with standard patterns

1   2   3   4   5

>10-14Å

| No change rational sequence of higher orders | Collapses to ~10Å | Collapses to 10Å | | 060 near 1.54Å | Regularly interstratified vermiculite-mica 17/ |
| No change | No change or slight increase in intensity | | 060 near 1.54Å | Regularly interstratified chlorite-mica 17/ |

| No change irrational sequence | Collapses to ~10Å | Collapses to 10Å | | 060 near 1.54Å | Randomly interstratified vermiculite-mica 6/ 14/ |
| No change | No change or slight increase in intensity | | 060 near 1.54Å | Randomly interstratified chlorite-mica 6/ 14/ |

| Expands to higher spacing | Collapses to ~10Å | Collapses to 10Å | | 060 near 1.50Å | Interstratified montmorillonite-mica 11/ 3/ 18/ |
| | | | | 060 near 1.54Å | Interstratified trioctahedral montmorillonite-mica 11/ 3/ 18/ |

| No change | Slight collapse | Further collapse | | 060 near 1.50Å | Interstratified dioctahedral vermiculite-mica 11/ 12/ 14/ |

12-12.5Å → No change → Destroyed or reduced in intensity → Destroyed → Fibrous morphology → Check hkl's against standard → Sepiolite 8/

10.5Å → No change → Destroyed--may survive slightly lower temperature → Destroyed → Fibrous morphology → Check hkl's against standard → Attapulgite or palygorskite 9/

Flow chart for the identification of clay minerals with 001 diffraction maxima at 10-14, 12-12.5, and 10.5 angstroms on the air dried pattern. Chart shows the effect of ethylene glycol and heat treatments on the location of these peaks.

Sample

Disaggregation, fractionation

Clay <2µ   Silt 2-62µ   Sand >62µ

2-20µ   20-62µ

X-rays of oriented aggregates

X-rays of randomly oriented powders

6   7   8   9   10

Air dried   Treated with ethylene glycol at least ½ hr, 4 hrs. by vapor pressure method   Heated to 400°C at least ½ hr   Heated to 550°C at least ½ hr   Electron micrograph if required

if required

Non-clay minerals determined by comparison of patterns 6, 7, 8, 9 and 10 with standard patterns

1   2   3   4   5

~10Å → Symmetrical No change → No change → No change

060 near 1.50Å Check hkl's against standards for polymorphs → Mica, muscovitic, various polymorphs   11/ 20/ 14/

060 between 1.51Å - 1.52Å 5Å peak very weak → Glauconite or celadonite (Roscoelite if V bearing)   11/ 14/ 13/

060 near 1.54Å → Biotite, various polymorphs   11/ 19/

Unsymmetrical or slight shift either way → No change or slight sharpening

060 variable → Interstratified mica-montmorillonite, or mica-vermiculite "Illite"   14/

Expands to ~11Å → Collapses to ~7Å → Destroyed → Tubular morphology → 060 near 1.49Å → Endellite   4/ 10/

7Å → No change → No change → No change → Fibrous morphology → Check hkl's against standard → Chrysotile   4/ 1/

Platy morphology → Check hkl's against standard → Antigorite   4/ 1/

Increases in spacing or no change → Collapses to 7Å → Destroyed → Tubular morphology → 060 near 1.49Å hk bands present → Halloysite   4/ 10/ 2/

No change → No change → Destroyed → Platy morphology → 060 near 1.49Å hk bands present moderately broad 001's → Disordered kaolinite ("fireclay")   4/

Hexagonal morphology → hkl's resolved → Kaolinite

Dickite   Check against standard patterns   4/

Nacrite

Platy morphology → 060 near 1.54Å → Chlorite   Check increase in intensity of 14Å spacing

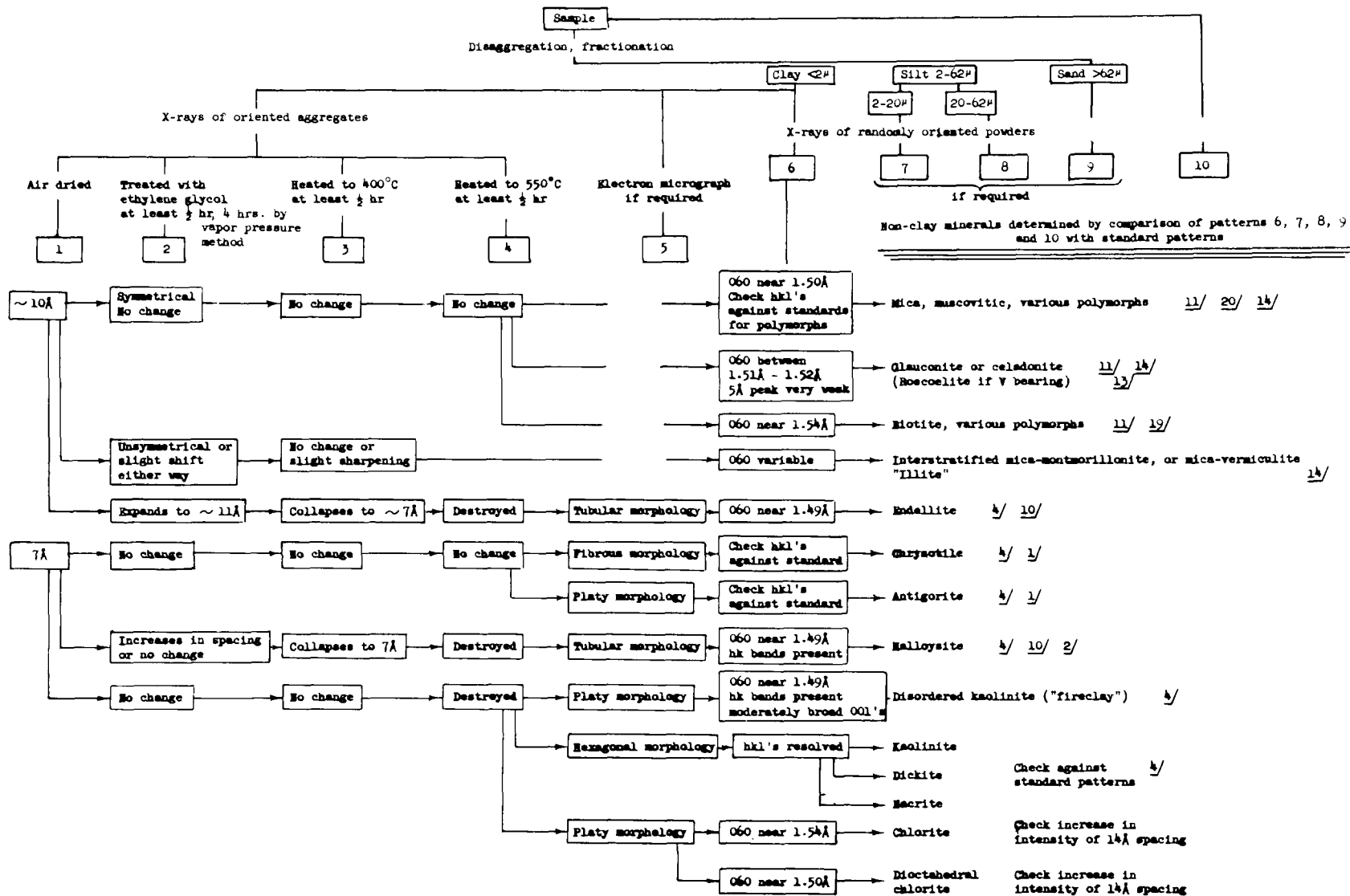060 near 1.50Å → Dioctahedral chlorite   Check increase in intensity of 14Å spacing

Flow chart for the identification of clay minerals with 001 diffraction maxima at 10 or 7 angstroms on the air dried pattern. Chart shows the effect of ethylene glycol and heat treatments on the location of these peaks.

APPENDIX G

Preparation of Glass Slides for Optical Microscopy

Preparation Of Glass Slides For Optical Microscopy

1. Materials required:

> mounting medium
> plastic dropper bottle
> felt marker pen with
>   water soluble ink
> spatula
> distilled water in a
>   dropper bottle
> hot plate
> glass cover slips
> glass microscope slides
> glass scribe

Pour a small amount of the mounting medium into the plastic dropper bottle. Any real or artificial (i.e. Piccolite or Caedex) canadian balsam may be used.

2. Mark the slide temporarily with the felt marking pen. A pen with water soluble ink is used because the mark is not soluble in xylene which may be necessary later to clean the excess mounting medium from the slide. Set the hot plate at about 300° F. The exact setting must be determined by tests; the cured mounting medium must no longer be tacky, but not be yellow or brittle.
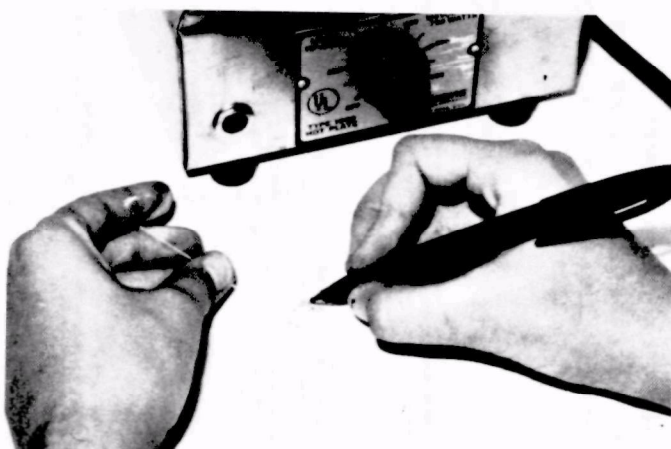
3. Place a small amount of sample in the center of the slide.
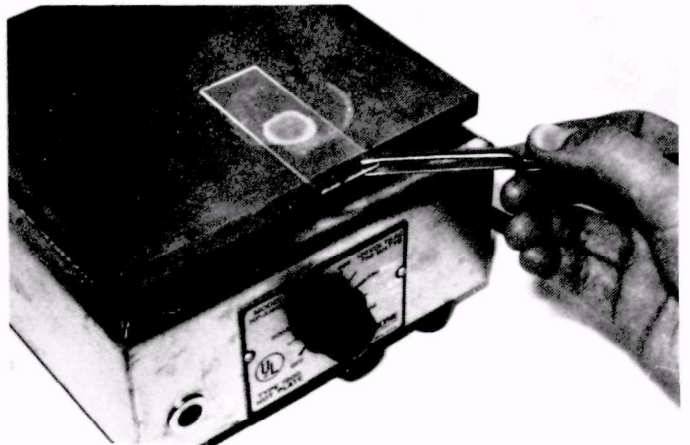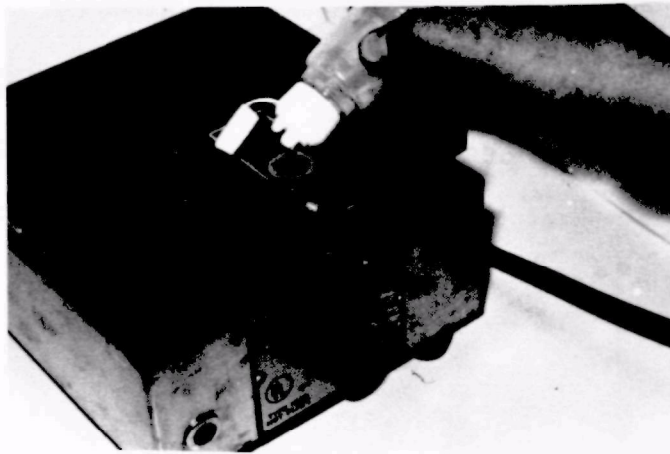
4. Add a drop of distilled water.
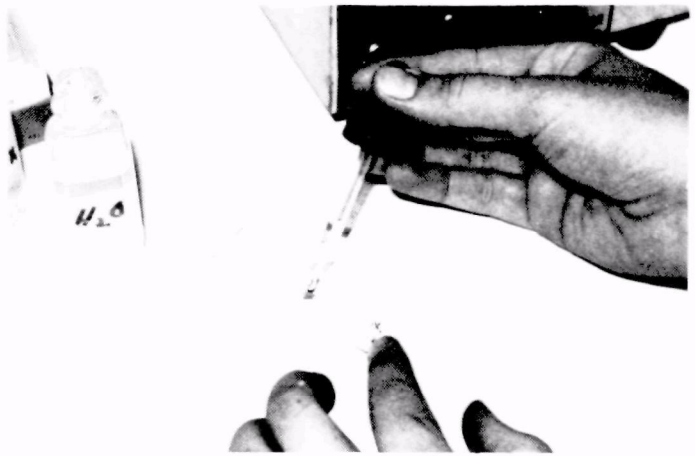
5. Mix and spread the sample with the spatula tip.
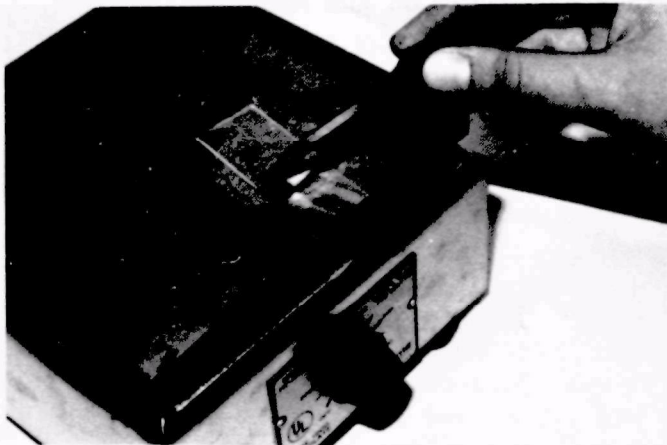

6. Place the slide on the hot plate to dry.

7. Place one or two drops of mounting medium on the center of the sample.

8. Place a square glass cover slip over the sample after the mounting medium has been allowed to cook for about one minute.


9. Press the cover slip down with a pair of forceps. The mounting medium should spread and fill the space beneath the cover glass.

10. If the mounting
    medium does not fill
    all of the space,
    add a drop right at
    the edge of the cover
    slip. Capillary
    action should draw the
    mounting medium under
    the cover slip.

11. Allow the slide to cook
    for another minute or
    two, then remove it from
    the hot plate and allow it
    to cool. If the slide has
    too much mounting medium,
    it can be cleaned with a
    razor and washed with
    xylene.
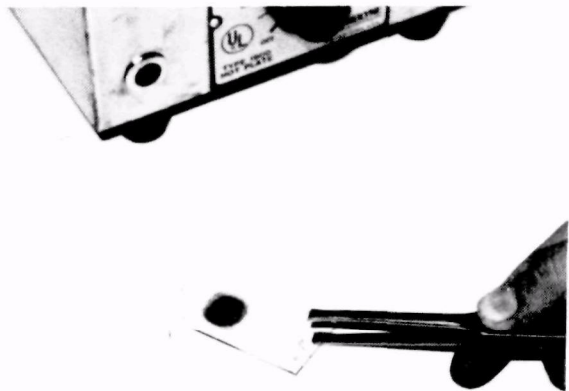
12. The slide should then be
    permanently marked with a
    glass scriber. This is not
    done earlier because glass
    chips would often end up in
    the sample and may be con-
    fused with volcanic glass
    shards.