



NBS TECHNICAL NOTE 929

U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

A Survey of Current Literature on Sampling, Sample Handling, and Long Term Storage for Environmental Materials

QC
100
U5753
NO. 929
1976
c.2

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards¹ was established by an act of Congress March 3, 1901. The Bureau's overall goal is to strengthen and advance the Nation's science and technology and facilitate their effective application for public benefit. To this end, the Bureau conducts research and provides: (1) a basis for the Nation's physical measurement system, (2) scientific and technological services for industry and government, (3) a technical basis for equity in trade, and (4) technical services to promote public safety. The Bureau consists of the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, the Institute for Computer Sciences and Technology, and the Office for Information Programs.

THE INSTITUTE FOR BASIC STANDARDS provides the central basis within the United States of a complete and consistent system of physical measurement; coordinates that system with measurement systems of other nations; and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. The Institute consists of the Office of Measurement Services, the Office of Radiation Measurement and the following Center and divisions:

Applied Mathematics — Electricity — Mechanics — Heat — Optical Physics — Center for Radiation Research: Nuclear Sciences; Applied Radiation — Laboratory Astrophysics² — Cryogenics² — Electromagnetics² — Time and Frequency².

THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to improved methods of measurement, standards, and data on the properties of well-characterized materials needed by industry, commerce, educational institutions, and Government; provides advisory and research services to other Government agencies; and develops, produces, and distributes standard reference materials. The Institute consists of the Office of Standard Reference Materials, the Office of Air and Water Measurement, and the following divisions:

Analytical Chemistry — Polymers — Metallurgy — Inorganic Materials — Reactor Radiation — Physical Chemistry.

THE INSTITUTE FOR APPLIED TECHNOLOGY provides technical services to promote the use of available technology and to facilitate technological innovation in industry and Government; cooperates with public and private organizations leading to the development of technological standards (including mandatory safety standards), codes and methods of test; and provides technical advice and services to Government agencies upon request. The Institute consists of the following divisions and Centers:

Standards Application and Analysis — Electronic Technology — Center for Consumer Product Technology: Product Systems Analysis; Product Engineering — Center for Building Technology: Structures, Materials, and Life Safety; Building Environment; Technical Evaluation and Application — Center for Fire Research: Fire Science; Fire Safety Engineering.

THE INSTITUTE FOR COMPUTER SCIENCES AND TECHNOLOGY conducts research and provides technical services designed to aid Government agencies in improving cost effectiveness in the conduct of their programs through the selection, acquisition, and effective utilization of automatic data processing equipment; and serves as the principal focus within the executive branch for the development of Federal standards for automatic data processing equipment, techniques, and computer languages. The Institute consists of the following divisions:

Computer Services — Systems and Software — Computer Systems Engineering — Information Technology.

THE OFFICE FOR INFORMATION PROGRAMS promotes optimum dissemination and accessibility of scientific information generated within NBS and other agencies of the Federal Government; promotes the development of the National Standard Reference Data System and a system of information analysis centers dealing with the broader aspects of the National Measurement System; provides appropriate services to ensure that the NBS staff has optimum accessibility to the scientific information of the world. The Office consists of the following organizational units:

Office of Standard Reference Data — Office of Information Activities — Office of Technical Publications — Library — Office of International Relations — Office of International Standards.

¹ Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.

² Located at Boulder, Colorado 80302.

1976

753

139

16

2

A Survey of Current Literature on Sampling, Sample Handling, and Long Term Storage for Environmental Materials^{technical note, 1976}

E. J. Maienthal and D. A. Becker

Analytical Chemistry Division
Institute for Materials Research
National Bureau of Standards
Washington, D.C. 20234



U.S. DEPARTMENT OF COMMERCE, Elliot L. Richardson, Secretary

Edward O. Vetter, Under Secretary

Dr. Betsy Ancker-Johnson, Assistant Secretary for Science and Technology

U.S. NATIONAL BUREAU OF STANDARDS, Ernest Ambler, Acting Director

Issued October 1976

National Bureau of Standards Technical Note 929

Nat. Bur. Stand. (U.S.), Tech. Note 929, 40 pages (Oct. 1976)

CODEN: NBTNAE

U.S. GOVERNMENT PRINTING OFFICE
WASHINGTON: 1976

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402
(Order by SD Catalog No. C13.46:929). Stock No. 003-003- Price **85 cents**
(Add 25 percent additional for other than U.S. mailing).

A Survey of Current Literature on Sampling, Sample Handling, and Long Term Storage for Environmental Materials

E. J. Maienthal and D. A. Becker

This article is the result of an extensive literature survey to establish optimum sampling, sample handling and long term storage techniques for a wide variety of environmental samples to retain sample integrity. The components of interest in these samples are trace elements, organics, pesticides, radionuclides or microbiologicals. This survey was done both manually and by use of various bibliographical retrieval services. Also the advice and opinions of workers in various aspects of the fields was obtained.

Key words: Environmental samples; long-term storage; microbiologicals; organics; pesticides; sample handling; sampling; chemical analysis; radionuclides; trace elements.

1. Introduction

In order to aid in the development of criteria for the possible establishment of a National Environmental Specimen Bank for the Environmental Protection Agency, a large portion of the recent literature concerning sampling and storage of environmental specimens has been examined. This has been done both manually and by use of bibliographical retrieval services such as Medline, Chemcon, Biosis, Cain, Defense Documentation Center and others. Also, the advice and opinion of workers in various aspects of the field has been obtained. A summary of the results of this survey is found below, separated into the various areas of concern.

2. Trace Elements

For trace elements there is an abundance of reports on sampling and storage (which should also apply to radionuclides); however, many of them are contradictory and should be further resolved by careful experimental work. Much of the published analytical data apparently is inaccurate because of such problems as gross sampling contamination or subsequent procedural contamination and failure to make proper blank corrections. Richards states that some oceanographers have permitted the perpetuation of the

notion that the concentrations of trace elements in the sea are well known, when, in fact, they are not (1)¹.

Patterson and Settle (2) report that the great mass of published lead data in plants, animal tissues and water is in error because of gross positive errors, and that the relatively large blanks usually present with lead concentrations less than a few $\mu\text{g/g}$ often makes the value obtained meaningless. Many trace element analysts, particularly in the field of oceanography and marine biology, believe that much of the previously published work is unreliable as a result of sample contamination. The values being reported are progressively lower as techniques are being improved. Hume reports that if a synthetic sea water were prepared from the purest reagent chemicals available, it would still be higher in many trace elements than natural sea water (3). Whitnack also has evidence to show that the reagents used are more contaminated than sea water (4). Speecke, et al. state that many chances exist for a biological material to be contaminated before it is analyzed (5); but few authors give the impression of the awareness of this and meaningless phrases are used, such as "metal-free" containers, "chemically clean" glass, etc., with no evidence to back it up. Berman states that one must never assume anything is acceptably free from trace metal contaminants until it has been tested (6).

It is felt that the materials, techniques, and expertise exist to provide viable long-term stored samples for most trace elements in most matrices; however, few in the field are using these techniques, partially because as Boutwell says, "...validity is an expensive commodity" (7).

The first consideration is the choice of the container and sampler composition and the method of cleaning and sampling. Murphy, Robertson, Thiers, Patterson, Tölg, and many others show results which indicate that rubber, neoprene, vycor, polyvinyl chloride, polystyrene, glass, polypropylene, linear polyethylene, platinum, etc., will introduce contamination in sampling and storage (8, 9, 10, 10a, 2, 11). Patterson recommends first, FEP Teflon, then ultra-pure quartz, conventional polyethylene or TFE Teflon containers. All cleaning and sample treatment should be done in laminar flow hoods or a clean room. He recommends cleaning with hot concentrated HNO_3 for three days, rinsing with high purity distilled water, followed by hot dilute 0.05 percent HNO_3 (both water and acid, prepared as described by Kuehner, et al. (12)) for one day, rinsing and heating with 0.05 percent HNO_3 five days, rinsing, then storing filled with 0.05 percent HNO_3 , wrapped in cleaned polyethylene until ready for use. (The two dilute HNO_3 leachings have

¹ Figures in parentheses indicate the literature references on page 16.

not been found necessary by some other workers). When ready for use, the containers can be thoroughly rinsed and dried in laminar flow hoods. Cleaned plastic gloves are worn in all phases of cleaning, sampling, etc. (2). Berman found that even after thorough cleaning and scrubbing of fingers, 0.1 to 0.4 μg of lead could still be washed off. Washings from a chain smoker give results of 0.3-4 μg of lead (6).

Karin, et al. report a three-day leach of polyethylene in either 8 or 16 M HNO_3 was necessary to remove certain trace metal contaminants (13).

Sampling implements Patterson recommends are either Teflon or Teflon-encased, except for frozen tissue sampling where a series of HNO_3 -acid cleaned stainless steel blades are used with very elaborate sampling procedures to remove areas contaminated by the blade (2). All of these type operations should be done in laminar flow hoods or clean room conditions.

Deionized water which has not been followed by distillation should not be used in any stages of the cleaning, sampling, or analysis as organic breakdown products may be formed, complexing some of the trace elements (8).

Numerous types of water samplers have been devised. Segar, et al. have described water sampling with Niskin bottles with rubber coated springs, Teflon coated coil springs and a new design Niskin bottle without internal closures. All gave trace metal contamination except the latter (14). Since Teflon is rather porous, apparently some metal diffusion through the spring coating must have occurred.

Harrison, et al. have designed a Teflon cylindrical sampler with a mechanism for opening both ends after submersion to the desired depth to avoid contamination from the water surface (15). It is attached to a metal frame and rudder which have a baked-on Teflon coating. It is also adapted so that the sample may be filtered immediately in an attached container holding a precleaned polyethylene bag in which the sample can be immediately sealed and frozen in liquid nitrogen. If the water sample is to be filtered, Morrison and Pierce, and many others suggest that it is best to do it immediately (16). The filter must be thoroughly precleaned, rinsed, and stored in cleaned polyethylene bags.

The sample chamber used by Patterson (2) consists of accordion pleated Teflon tubing, the entry port being protected by a bath of ultra pure water (prepared as already mentioned). At the deep water sampling depth desired, a

trigger retracts the water bath shroud and ruptures the end diaphragm which contains the pure water. The water sampler is lowered continuously so that it is continually dropping into virgin water. After a short interval to allow the bath water to be washed away, a second trigger expands the sample accordion bag and seals the entry port.

The storage of aqueous samples presents an even greater challenge as most samples start undergoing changes the instant they are sampled. Pre-aging the sampler and sample container with some of the same sample would be desirable whenever possible. Amore states that losses as high as 50 percent can occur during one hour of storage (17). An EPA manual on methods of water analysis says that complete and unequivocal preservation of samples is a practical impossibility, that complete stability can never be obtained, and that preservation techniques only retard the chemical and biological changes that continue after the sample is taken (18). The methods of preservation are intended to retard biological action, retard hydrolysis of chemical compounds and reduce the volatility of the components. Their recommended methods include pH control, chemical addition, refrigeration, and freezing.

Although there is much in the literature on relatively short term storage of different aqueous (non-frozen) solutions under varying conditions, there are many disagreements and most of the results do not look favorable for long term storage. A USGS manual for water analysis says that the shorter the time that elapses between the collection of a sample and its analysis, the more reliable will be the results (19).

Pettis and Phillip give an excellent review of the literature on trace metal analysis in sea water. They discuss sampling and cleaning procedures, sample pretreatment, standard reference materials, and analytical method of determination of the trace metals (19a).

Robertson found that sea water adjusted to pH 8 stored in polyethylene resulted in a 90 percent indium loss in 20 days and a 90 percent loss of iron in 55 days (20). Hummel found that 75 percent of the gold in sea water was lost after three weeks in polyethylene (21). King, et al. found that less than 3 percent of the cadmium was lost to polyethylene at pH's of 3 to 10 after two weeks storage (22). West, et al. (23) found more silver adsorption on glass at pH 4 than at pH 7, a significant decrease occurring at pH 7, and a rise at pH 8, and they also state that pyrex showed more erratic adsorption patterns than polyethylene or silicone-coated containers. Struempfer (24) states that acidi-

fication with nitric acid to pH 2 prevents adsorption of silver, lead, cadmium, and zinc on pyrex, and silver on polyethylene. Dyck (25) reports lack of confirmation with the work of West, et al. with silver, and states there is a direct increase in silver adsorbed on glass with increase in pH. He also states that for periods over several months, plastic adsorbed more silver than glass. Lai and Weiss (26) found no silver loss when sea water was stored in polyethylene and acidified to a pH of 3.5 to 4.0 with acetic acid. King, et al. (22) found losses as high as 75 percent for cadmium when stored in glass at pH 9. Eichholz, et al. (27) compared adsorption of a number of elements on pyrex and polyethylene and state that pyrex is preferable to polyethylene; however, they found less contamination for cesium, ruthenium, and zirconium when using polyethylene. Smith (28) studied stability of a number of ions including cadmium, antimony, tin, and lithium, and states that of the elements studied only lithium was stable over the pH range of one to 11. He therefore recommends acidification to pH one. In another report (29), he states that freezing the liquid samples as soon as they are collected is an excellent solution for the adsorption problem. The losses may be due to adsorption or also to precipitation or particulate formation. Salman also states that freezing can be used to preserve the water samples at the collection site (29a).

Rattonetti examined the stability of a large number of trace metals in a variety of water matrices stored in polyethylene at differing pH's and concluded that loss to container walls is insignificant compared to losses to the particles present in natural aqueous systems (30).

Moody, et al. prepared two mercury-in-water Standard Reference Materials at the 1 ppm and 1 ppb level which have been stable for over a year in both glass and polyethylene (31). This was achieved by the addition of 1 $\mu\text{g/g}$ and 10 ng/g of Au^{+3} , respectively, and 0.5 N nitric acid. Lo and Wai verified this for shorter term storage with 0.2 $\mu\text{g/g}$ Au^{+3} and nitric acid at pH 0.5 (32), but were unable to confirm Feldman's stabilization with potassium dichromate (33) or the report of Issaq and Zielinski with hydrogen peroxide (34). Avotins and Jenne state that the biological effects have been overlooked in many mercury in water investigations, and as a result of unpredictable growth of bacterial and yeast populations, with production of metabolites, mercury may either vaporize, bind to the walls of the vessel or be stabilized in solution (35). Huey, et al. have reported that cadmium can be volatilized from its inorganic salts by a microorganism through conversion to a volatile organic compound (36). The volatilization is stimulated by vitamin B_{12} . Methylmercury formation by this organism is

also stimulated by B_{12} , the absence of which causes the organism to form metallic mercury from inorganic mercuric salts. In samples where this type of reaction occurs, freeze-drying is not advisable as a method of sample preservation. For long term preservation for trace-element analysis, freezing and possibly freeze-drying for most elements (probably followed by radiosterilization), would seem to be the most likely alternatives. Morrison and Pierce state that freezing may be a suitable preservation technique for trace elements but has not been adequately tested to date (16). Allen, et al. recommend immediate freezing at -10 to -15°C to prevent microbiological changes in soluble mineral and silica concentrations (37); however, for long term storage, immediate freezing in liquid nitrogen as recommended by Harrison, et al. (15) and others (29), followed by freeze-drying for most trace elements (and radiosterilization) or storage at -70° to -80°C would seem preferable. Low temperature (oxygen plasma) ashing and dry ashing are also possibilities in some cases.

Harrison, et al. (38) and Filby, et al. (38a), have reported that radioisotope studies of the volatile elements such as arsenic, antimony, selenium, bromide, and mercury have shown no significant losses in water samples which have been freeze-dried.

Heron studied the determination of phosphate in lake water before and after freezing (39). It was expected that rapid freezing would cause cell rupture resulting in higher phosphate values, but this did not occur. Varying phosphate values were found whenever growth of bacteria was occurring. This was prevented by pre-cleaning the sample bottle with a solution which is 5 percent in iodine and 8 percent in potassium iodide and immediate freezing of the water sample.

Philbert found that in freezing lake water samples soluble reactive silica and phosphorus concentrations were decreased in the thawed samples (40). A decrease in total alkalinity and dissolved chloride was also observed. Inconsistent changes were observed for ammonia and the various forms of nitrogen.

A USGS manual on methods of water sampling recommends that water samples for inorganic analysis should not be frozen (19); however, there is sufficient reason to expect that if the process is performed properly, freezing is acceptable for most trace elements. The samples should be subsampled before freezing, because once thawed, they should not be refrozen. The entire subsample should then be taken for analysis. They should be frozen in one of the container materials already discussed, under a gas such as nitrogen or

argon to prevent sample oxidation. They should be sealed in at least 2 and possibly 3 [as Patterson recommends (2)] series of plastic bags. Since most plastics are porous (41), they should then be placed in a tightly sealed glass container containing nitrogen or argon with minimum void space, followed by storage in the dark at -70°C . Bothner and Robertson (42) have reported that sea water samples stored in polyethylene containers have picked up mercury from being stored in a room contaminated with metallic mercury. This has been verified in a closed chamber with pools of clean mercury surrounding a mercury solution in Teflon and polyethylene bottles, but has not as yet been verified in an ordinary laboratory atmosphere where spilled mercury would probably be covered with dust, thus effectively diminishing its vapor pressure (43).

When the frozen water sample is used, the whole sample should be used because of possible selective ion incorporation in the ice (44). The walls of the inner container will probably have to be washed with acid to remove any hydrolyzed or adsorbed material.

The possibility of losing organic or inorganic mercury during freeze-drying of biological materials was investigated by LaFleur, as Pillay, et al. had published data indicating losses (45). LaFleur found no losses for inorganic or naturally bound methyl- or phenylmercury in tissue and blood; however, for aqueous solutions, losses of up to 90 percent could occur for organic and up to 10 percent for metallic mercury (46).

3. Biological-Tissue and Fluids

For tissue and biological fluid sampling, the sampling device presents considerably more difficulties. The use of a laser beam for cutting bone by Hislop and Parker (47) offers many interesting possibilities. Some loss of trace elements on the surface may occur but would be negligible with regard to the entire sample. A quartz or glass knife should also be suitable for many kinds of tissue. Montgomery, et al. used a glass knife to cut fish in small pieces for the determination of iron, zinc, lead, cadmium, copper, and manganese (48). A problem here is the chipping of the cutting edge; weighing the knife before and after use may indicate if this difficulty arises.

Most workers use stainless steel implements. However, this is fraught with dangers of contamination for many trace elements even when done as carefully as described by Patterson earlier (2). Versieck, et al. report on the contamination introduced during needle biopsies of liver (49). They state that steel surgical blades lead to somewhat less contamination,

but are not suitable for some trace elements such as chromium and nickel. The needle biopsies resulted in contaminations of as much as 1.7 ppm of copper, 0.64 ppm of manganese, 11 ppm of chromium, 12 ppm of nickel, 20 ppm of iron, 0.24 ppm of cobalt, 0.012 ppm of silver, 0.46 ppm of tin, 0.069 ppm of antimony and 1.2 ppm of tantalum. Speeche, et al. have reported on the sampling and storage of biological materials for contamination by chromium, manganese, nickel and cobalt by drawing 4 series of 20 ml portions of blood using disposable needles (5). For manganese, the first 20 ml showed contamination of 0.2 ppb, the fourth, 0.02 ppb; for chromium, the first 85 ppb, the fourth 15 ppb; for nickel, the first 71 ppb, the fourth 12 ppb; for cobalt the first 0.9 ppb, and the fourth 0.2 ppb. They also compared contamination introduced in another series of liver samples using Meneghini biopsy needles and surgical blades. For the needles, they found contaminations of as much as 600 ppb of manganese, 9000 ppb of chromium, 12,000 ppb of nickel and 230 ppb of cobalt; for the surgical blades, 3 ppb of manganese, 15 ppb of chromium, 60 ppb of nickel, and 1 ppb of cobalt. They discuss the possibility of using laser beams on hard and soft tissues and platinum-rhodium alloy needles; however, it is preferable that the platinum needles have Kel-F hubs to avoid contamination. For storage, Speeche, et al. recommend immediate, rapid freeze-drying, but point out that some volatile materials may be lost. All the work should be done in a clean-room type laboratory with no exposed metal parts which might cause contamination.

Fisher, et al. (50) also reported that serum samples should be quickly frozen with as little air space as possible (as described earlier, the air should be displaced with nitrogen or argon). They also checked storage at room temperature, 8°C and -15°C. No differences for calcium, magnesium, copper, zinc, sodium, and potassium were noticed up to 16 days. Essentially no changes were observed in the refrigerated and frozen samples up to 50 days, but changes did occur in the samples stored at room temperature. Longer term storage would probably also result in changes in the refrigerated samples. Some microorganisms can grow in a temperature as low as -6°C (51).

In a discussion of sampling for clinical chemistry, Ibbott recommends separating the serum from the clot as soon as possible to avoid contamination from cell leakage (52). He also states that the majority of the serum components are stable indefinitely in dry ice (about -70°C), and that the samples exhibit concentration gradients due to freezing and must be thoroughly mixed after thawing. Omang and Vellar also point out the concentration gradients obtained after freezing and thawing serum, sweat, and urine. They found top-bottom differences of thawed samples of up to one hundred (53).

4. Museum Specimens

The futility of trace element analysis of museum type specimens stored in preservatives has been pointed out by a number of authors. Bowen and Sutton in analysis of marine sponges found that nickel accumulation in the preservative occurs quite frequently in these types of samples (54). Gibbs, et al. investigated the effects of time and preservatives on museum fish specimens and found no evidence to support the theory that preserved museum specimens can provide reliable estimates of heavy metal concentrations (55). They tested many types of preservatives such as ethanol, formalin, isopropyl alcohol, etc., and found interaction with the specimens in all cases. These solvents may either leach trace metals from the specimen or contaminate the specimens by heavy metals contained in the preservatives or container. In many cases, metal identification tags are placed in with the preservative, which contribute even further to the contamination of the sample. In some instances, the trace metal content increased over the years and in other cases, decreased from leaching even in a short period of time, such as a month.

A possible exception for the museum type specimens are those which have been stored in relatively clean, dry areas not subject to leaching or contamination. Cockburn, et al. (56) describe the autopsy of an Egyptian mummy, Pum II, which included the analysis of some trace elements in bone by R. G. Smith (57). He found 0.6 ppm of lead and 0.43 ppm of mercury. The lead content of modern bone averages 6.55 to 18 ppm (58). Assuming no leaching has occurred, it would appear, on the basis of limited sampling, that man's environment has contributed considerably to his lead body burden. The mercury level, however, is relatively unchanged, that of modern bone averaging about 0.45 ppm (59).

5. Crustal and Botanical Materials

The sampling and storage of soils, rocks, minerals, sediments, and plants does not present quite as many problems as the matrices already discussed, but more precautions should be taken than are generally observed. Morrison and Pierce (16) state that the use of a spade to sample soil is preferable to a soil auger and that dry samples can be collected in a clean cloth bag, but this procedure would certainly lead to contamination for some trace metals. Clean Teflon encased tools as recommended by Patterson and Settle (2) should be used except for most plants which can be picked with clean plastic gloves. It appears that soils and sediments with any significant water content (especially sediment samples) should be frozen in such a way that no water loss can occur, and stored as recommended for water samples.

There are many papers in the literature which indicate that soils and sediments undergo changes in structure and chemical state even when dried at room temperature. This should not have a great effect on the total trace element content in most cases, but if speciation, organic extractable trace elements, etc., are of interest, any form of drying may invalidate the sample. Attoe (60) reports that potassium may be fixed in a nonexchangeable form when a potassium-fertilized soil is air-dried. Air drying of unfertilized soils resulted in a 4-90 percent increase in exchangeable potassium when the soils are remoistened. Schalsha, et al. (61) state that air drying produces significant irreversible changes in volcanic ash soils. For instance, soil samples with a clay-type texture in the field, change to a sandy texture with air drying. Air drying also reportedly markedly affects cation exchange capacity, soluble phosphorus and iron, and decreases the pH slightly. Air drying decreased the total exchangeable and acid soluble iron, but increased the chelatable iron extracted by salicylate. The mechanical and chemical analysis of volcanic ash soils more accurately indicate field conditions when samples contain the original moisture at field capacity.

Barrow (62) found when soils were dried, inorganic sulfate immediately increased (probably as a result of decomposing organic sulfates in the soil becoming immediately available to the plants). Even when two different soils are dried at the same temperature, the relative availability of the sulfur may be no indication of the relative availability when they were fresh.

Harpstead and Brage (63) reported that the drying and storage of soils leads to a pronounced increase in their nitrifying ability because of the changes in the relative numbers of various microorganisms in the soil. Birch found that when remoistening dried soil, the first rapid decomposition slows down and this pattern is repeated during successive dryings and wettings (64). The magnitude of the decomposition depends on the amount of carbon in the soil and on the drying conditions, air drying being less effective than oven drying. Vacuum drying and oven drying gave the same moisture loss results, but oven drying gave a much greater amount of decomposition on rewetting.

Birch (65,66) also states that the longer a soil is kept air dried, the greater the amount of water-soluble and organic material that can be extracted, even though it does not lose additional moisture, and also the greater the amounts of carbon and nitrogen are mineralized on remoistening. He also finds greater effects if the soil is dried at 100°C, possibly because of increased gel porosity and

surface area, and possibly because of increased microbiological activity occurring during the remoistening of the dried soil.

Nevo and Hagin (67) state that the changes occurring after three months of air drying storage was independent of microorganisms. The major factor is the change in the physical structure of the organic fraction. They found a good correlation between the nitrification rate and the surface area of particles of an organic soil.

Hesse (68) states that oven drying a soil, despite its reproducibility, should not be recommended, because of the profound changes caused. Also he says that storing a soil in a moist state has the effect of incubating it, but without temperature or moisture control, resulting in a build-up of carbon dioxide at the expense of oxygen. As such treatment results in many complicated reactions, it is most undesirable to keep a soil in a moist state for any length of time for the purpose of analysis. He also reports on investigations of J. M. Coleman (private communication) that moist soil samples stored in plastic containers can result in fundamental changes in clay minerals. It is thought that an organic complex passes from plastic into the clay mineral. All these references seem to point out that drying or freeze-drying may result in irreversible changes which will affect also the complexation state of the trace metals and that freezing at -70°C to -80°C as recommended earlier should be the method of storage.

Plant sampling can probably be done by picking with plastic gloves and storing by freezing in containers as already mentioned, with care to avoid moisture loss.

Arkeley, et al. (69) state that trace elements such as carried by peat dust deposited on plants are easily washed off (high purity distilled water should be used) but those deposited by sprays are not, because of partial absorption in the leaf. Lagerwerff (70) found increases in absorption of cadmium, zinc, and lead on leaf surfaces probably enhanced by drying.

Work by Koeppe and Miller (71) showed a much higher uptake of lead by maize roots than in the stems or leaves. Washing with distilled water removed little lead, but washing with EDTA solution removed about 90 percent of the lead, indicating the lead is largely retained on the exterior surface of the roots.

For sampling of air particulates, Patterson and Settle (2) recommend cleaning Millipore or Nucleopore filters by soaking in cold 6N HCl two days, rinsing on a cleaned

polyethylene Buchner funnel with high purity distilled water, soaking two days at 55°C with 1 percent NH_4F (prepared by neutralizing high purity NH_4OH with high purity HF) followed by rinsing with high purity water. These operations, of course, are carried out in a clean room atmosphere or laminar flow hoods. The filters are then stored in cleaned polyethylene bags or boxes. The lead blank on these filters was found to be less than 1 ng/47 mm filter.

6. Organics and Pesticides

With the exception of the use of plastic gloves for sampling to avoid contamination from body oils (72), storage containers and implements for trace organics and pesticides definitely must not be plastic of any kind, with the possible exception of Teflon, as plastic is known to both introduce interferences and sorb pesticides (and organics) (73,73a). Many examples are given in the literature which show that additives such as plasticizers, organometallic or other stabilizer antioxidants, colorants or other components are leached from the plastic and contaminate the sample (74).

Some polyvinyl chloride tubings were shown to release a constituent to some systems containing alcohol, propylene glycol or polyethylene glycols (75). Gibbs found that asbestos fiber was highly contaminated by 3,3'-5,5'-tetra-tertiary butyl diphenoquinone after storage in polyethylene bags (76). Lipids in soil samples stored in standard plastic lined canvas bags were found to take up phthalate esters and other contaminants from the plastic (77).

Most workers in the field recommend storage in glass containers with Teflon or aluminum foil lined caps (72,73, 73a,78); however, it has been reported that Teflon sheet and aluminum foil have been found to contain up to 400 and 300 ppb, respectively, of di-2 ethylbutyl phthalate (79,80).

Hertz, et al. (81) recommended cleaning the glassware with soap and water, then in concentrated H_2SO_4 at 100°C for 30 min and finally rinsing with specially prepared distilled water made by redistilling the house distilled water over KMnO_4 -KOH. The distillate is then passed through an XAD-2 column, and the water is redistilled to remove any particulates from the XAD-2 resin. Finally, the bottles are then rinsed with methanol and triple-distilled pentane, and filled with nitrogen from a liquid nitrogen source and sealed.

Others recommend wrapping the cleaned glassware in aluminum foil and heating at 625°C for four hours (82). The maintenance of high quality distilled water can be a problem as some microorganisms can grow rapidly in distilled water

and some chemical reagents (82,83,84). It is reported by Hamilton and Myoda (82) that the amino acids, proteins and bacteria often found in some laboratory reagent solutions and distilled water, are probably airborne and enter the outlet of the stills or deionizing systems where they multiply. A method of catalytic pyrodistillation has been reported to remove organic impurities not removed by ordinary or oxidative distillation because of the steam volatility of the compounds or their derivatives (85).

It has been recommended in sampling that "an analyst or person directly concerned with the particular study should collect the samples. Inexperienced personnel should never be allowed to collect the samples unless they are very closely supervised" (78). This, of course, is true to all types of environmental sampling.

When sampling marine organisms and sediments for organics or pesticides, most workers recommend freezing immediately in dry ice or liquid nitrogen (72,81) and final storage at about -70° to -80°C (86) in the dark. Breakdown of pp'-DDT to pp'-TDE in Bengalese finch liver, and breakdown due to other biological processes have been reported at home freezer storage conditions (approximately -14°C) (87,88).

Bristol reported in a study of pesticide residues in potatoes that metabolically incorporated 2,4-D untreated potato samples stored whole at 4°C decreased over a period of 15 months, while those of 2,4-DCP remained constant. Recoveries of 2,4-D from frozen samples were constant over a 15-month period, but those of 2,4-DCP decreased slowly from 88 to 47 percent. The 2,4-DCP samples stored in plastic bags gave a characteristic odor, indicating the losses were due to volatilization from the frozen samples (89).

It is reported by the Federal Working Group on Pest Management that increased knowledge of sample contact with various kinds of synthetic wraps and containers demonstrates the necessity for glass and perhaps aluminum foil to preserve the integrity of wet samples. Immediate freezing and maintenance of the frozen sample until analysis is the best way to protect samples and prevent degradation and loss of pesticide residues (73). (This also is undoubtedly true for all organic components.) They also state that pesticides can migrate to the walls of a container and be adsorbed; hence, even with a glass container, after the sample is poured out, the walls should be rinsed with the solvent in case the extraction is not made in the container itself (this should also apply to any organics).

There is evidence in the literature that samples to be analyzed for organics or pesticides cannot be dried or

freeze-dried without danger of some loss. One study showed 79 percent loss of lindane, 37 percent for dieldrin, 57 percent for p,p'-DDT and 31 percent in o,p'-DDT-DDD on whole eggs and 50 percent for lindane in egg yolk when samples were frozen at -23°C, freeze-dried for 24 hr, and transferred and stored in sealed glass vials at 4°C, so that there was no volatility loss in storage (90).

Morris found that preservation of zooplankton in formalin and methanol resulted in hydrolysis of the animals' lipid and degradation of polyunsaturated fatty acids (90a). He found that the samples were stable up to nine months if stored deep frozen under nitrogen.

Smith reports that changes in nonstructural carbohydrate concentrations occur during the storage of either heat or freeze-dried tissues and concluded that no preservation method is as good as the immediate analysis of fresh tissue; however, he did not investigate straight freezing (91). Other workers found losses in higher fatty acids under either oven or freeze-drying conditions after storage for nine months (92).

Dessicants for tissue preservation are used by some workers who are unable to freeze their samples. The samples are chilled, homogenized, and blended with a combination of sodium sulfate and powdered silica. It is stated that the resulting mixture is a dry, free-flowing powder wherein the pesticide residues are stable for 15 days or more at room temperature (73).

7. Microbiologicals

Microbiologicals or cellular organisms consist of many different types such as algae, protozoa, fungi (molds or yeasts), bacteria, submicroscopic viruses and other (microscopic nematodes, some insects and some crustaceans), necessitating a wide variety of different sampling and storage conditions. Most preservation has been done through culturing and subculturing. With care, these have been maintained for 5-8 years (93). The sampling implements and containers should obviously be sterile and glass is preferred to plastic, since bacteria tends to grow on plastic surfaces. Since all known life forms require water in the liquid state, this automatically limits the temperature range for microorganisms. Both bacteria and viruses can be freeze-dried to maintain culture collections and to preserve them for use as vaccines. Insects have been supercooled to -30°C without apparent damage; however, they die if ice crystals are formed. Mouse embryos have survived deep freezing to -196°C. Freezing is accompanied by the removal of water, so the cell is subject to damage by both freezing and drying.

Mechanical injury is caused by ice crystals and the removal of the water causes an increase in dissolved substances. Biochemically debilitated cells may show a reduction or complete loss of some enzymes, and ice-damaged cells may have leaky membranes or an altered structure. The damage from freezing, drying, and thawing can range from essentially none to 100 percent, depending on the specific organism and conditions. Spores are resistant to both cold and drying. Rapid freezing is reported to be usually better with bacteria, whereas slow freezing is better for animal cell survival. It has been stated that rapid thawing gives better survival than slow thawing (51). Fleischer and Kervina report in studies on long-term preservation of liver for subcellular fractionation that rapid freezing and thawing minimizes the time in which degradation can occur (94). Repeated freezing and thawing is more harmful. Freeze-dried bacteria are better kept at refrigerator temperature than at room temperature (51).

McPeak and Camp (94a) have reported on work of Valeri, et al. (95), Meryman and Hornblower (96), and Gibson, et al. (97). Their studies on storage of red blood cells show that if the samples are stored at a higher temperature than -60°C , they deteriorate within a few weeks. If glycerol is used as a cryoprotective agent and the cells are frozen rapidly in liquid nitrogen and stored at -80°C , the cells are reported to be stable for over 10 years. Fluctuations in storage temperatures of not more than 10°C above or below -80°C are reported to have no adverse effect. Farrant, et al. (98) report that improved recovery of frozen cells can be obtained by interrupting rapid cooling with a timed exposure to a single subzero temperature.

There is a vast amount of additional information in the literature on the subjects of sampling, handling, and storage for microbiologicals, blood, and other biological samples. Since there are so many different types of species and the related optimum handling appropriate to each species, it is difficult to summarize; however, a number of additional references are given below to indicate the type of problems that are encountered as well as some additional references concerning other subjects discussed above.

References

1. F. A. Richards, On the State of Our Knowledge of Trace Elements in the Ocean, *Geochim. Cosmochim Acta*, 10, 241-243 (1950).
2. C. C. Patterson and D. M. Settle, The Reduction of Orders of Magnitude Errors in Lead Analyses of Biological Materials and Natural Waters by Evaluating and Controlling the Extent and Sources of Industrial Lead Contamination Introduced During Sample Collecting, Handling, and Analysis, NBS, TS.*
3. D. N. Hume, "Pitfalls in the Determination of Environmental Trace Metals," in *Progress in Analytical Chemistry*, Vol. V, Ed. S. Ahuja, E. M. Cohen, T. J. Kneip, J. L. Lambert, and Gunter Zweig, pp. 3-16, Plenum Press, New York, London (1973).
4. G. C. Whitnack, Application of Single-Sweep Polarography to the Analyses of Trace Elements in Sea Water, *Polarography*, 641-651 (1964).
5. A. Speecke, J. Hoste, and J. Versieck, Sampling of Biological Materials, NBS, TS.*
6. E. Berman, The Challenge of Getting the Lead Out, NBS, TS.*
7. J. H. Boutwell, Jr., Accuracy and Quality Control in Trace Element Analysis, NBS, TS.*
8. T. J. Murphy, The Role of the Analytical Blank in Accurate Trace Analysis, NBS, TS.*
9. D. E. Robertson, Role of Contamination in Trace Element Analysis of Sea Water, *Anal. Chem.*, 40, 1067-1072 (1968).
10. R. E. Thiers, Separation, Concentration and Contamination in Trace Analysis, Ed. J. H. Yoe and H. J. Koch, Jr., pp. 637-666, Wiley, New York (1957).
- 10a. R. E. Thiers, Contamination in Trace Element Analysis and Its Control in Methods of Biochemical Analysis, Ed., D. Glick, Vol. V, pp. 273-333, Interscience Inc., New York (1957).
11. G. Tölg, Extreme Trace Analysis of the Elements-I, Methods and Problems of Sample Treatment Separation and Enrichment, *Talanta*, 19, 1489-1521 (1972).

12. E. C. Kuehner, R. Alvarez, P. J. Paulsen, and T. J. Murphy, Production and Analysis of Special High-Purity Acids Prepared by Sub-Boiling Distillation, *Anal. Chem.*, 44, 2050-2056 (1972).
13. R. W. Karin, J. A. Buono, and J. L. Fasching, Removal of Trace Elemental Impurities from Polyethylene by Nitric Acid, *Anal. Chem.*, 47, 2296-2299 (1975).
14. D. A. Segar and G. A. Berberian, Comparisons of Sample Contamination by Pumping Systems, Niskin Bottles with Rubber and Teflon Coated Coil Springs, and New Niskin Bottles Without Internal Closures, Paper presented at the 168th ACS National Meeting held in Atlantic City, N. J., September 1974.
15. S. H. Harrison, P. D. LaFleur, and W. Zoller, Sampling and Sample Handling for Activation Analysis of River Water, NBS, TS.*
16. G. H. Morrison and J. O. Pierce, Sampling, Sample Preparation and Storage for Analysis, in *Geochemistry and the Environment*, Vol. I, pp. 90-97, National Academy of Sciences, Washington, D. C. (1974).
17. F. Amore, Losses, Interferences and Contamination in Trace Metal Analysis - Some Examples, NBS, TS.*
18. U. S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, p. VI, Office of Technology Transfer, EPA (1974).
19. Federal Interagency Work Group on Designation of Standards for Water Data Acquisition, Recommended Methods for Water Data Acquisition, p. V-10, U. S. Department of the Interior, Geological Survey, Office of Water Data Acquisition (1972).
- 19a. R. W. Pettis and A. T. Phillip, Trace Analysis of Heavy Metals in the Marine Environment, Rept. 619, Australian Defence Scientific Service, Materials Research Laboratories, Maribyrnong, Victoria, December 1974.
20. D. E. Robertson, The Adsorption of Trace Elements in Sea Water on Various Container Surfaces, *Anal. Chim. Acta*, 42, 533-536 (1968).
21. R. W. Hummel, Determination of Gold in Sea Water by Radioactivation Analysis, *Analyst*, 82, 483-488 (1957).

22. W. G. King, J. M. Rodriguez, C. M. Wai, Losses of Trace Concentrations of Cadmium from Aqueous Solution during Storage in Glass Containers, *Anal. Chem.*, 46, 771-773 (1974).
23. F. K. West, P. W. West, and F. A. Iddings, Adsorption of Traces of Silver on Container Surfaces, *Anal. Chem.*, 38, 1566-1570 (1966).
24. A. W. Struempfer, Adsorption Characteristics of Silver, Lead, Cadmium, Zinc, and Nickel on Borosilicate Glass, Polyethylene, and Polypropylene Container Surfaces, *Anal. Chem.*, 45, 2251-2254 (1973):
25. W. Dyck, Adsorption of Silver on Borosilicate Glass-Effect of pH and Time, *Anal. Chem.*, 40, 454-455 (1968).
26. M. G. Lai and H. V. Weiss, Determination of Silver in Sea Water, *Anal. Chem.*, 34, 1012-1015 (1962).
27. G. G. Eichholz, A. E. Nagel, and R. B. Hughes, Adsorption of Ions in Dilute Aqueous Solutions on Glass and Plastic Surfaces, *Anal. Chem.*, 37, 863-868 (1965).
28. A. E. Smith, A Study of the Variation with pH of the Solubility and Stability of Some Metal Ions at Low Concentrations in Aqueous Solution, Part II, *Analyst*, 98, 209-212 (1973).
29. Ibid., A Study of the Variation with pH of the Solubility and Stability of Some Metal Ions at Low Concentrations in Aqueous Solution, Part I, 98, 65-68 (1973).
- 29a. H. A. Salman, Trace Element Analyses in Waters Combining Solvent Extraction with the Atomic Absorption Microsampling Boat, Rept. Ch. E-102, Bureau of Reclamation, U. S. Department of the Interior, Denver, CO, July 1969.
30. A. Rattonetti, Stability of Metal Ions in Aqueous Environmental Samples, NBS, TS.*
31. J. R. Moody, P. J. Paulsen, T. C. Rains, and H. L. Rook, The Preparation and Certification of Trace Mercury in Water Standard Reference Materials, NBS, TS.*
32. J. M. Lo and C. M. Wai, Mercury Loss from Water During Storage: Mechanisms and Prevention, *Anal. Chem.*, 47, 1869-1870 (1975).

33. C. Feldman, Preservation of Dilute Mercury Solutions, Anal. Chem., 46, 99-102 (1974).
34. H. J. Issaq and W. L. Zielinski, Jr., Loss of Lead from Aqueous Solution During Storage, Anal. Chem., 46, 1328-1329 (1974).
35. P. Avotins and E. A. Jenne, The Time Stability of Dissolved Mercury in Water Samples, J. Environ. Quality (1975, in press).
36. C. W. Huey, F. Brinckman, W. Iverson, and S. O. Grim, Bacterial Volatilization of Cadmium, Proceedings of the International Conference on Heavy Metals in the Environment, October 27-31, 1975, Toronto (June 1976, in press).
37. S. E. Allen, H. M. Grimshaw, J. A. Parkinson, and C. Quarmby, p. 99 in Chemical Analysis of Ecological Materials, S. E. Allen, Ed. (Halstead Press), John Wiley and Sons, New York (1974).
38. S. H. Harrison, P. D. LaFleur, and W. H. Zoller, Evaluation of Lyophilization, for the Preconcentration of Natural Water Samples Prior to Neutron Activation Analysis, Anal. Chem., 47, 1685-1688 (1975)
- 38a. R. H. Filby, K. R. Shah, and W. H. Funk, Role of Neutron Activation Analysis in the Study of Heavy Metal Pollution of a Lake-River System, Proc. of the 2nd International Conference on Nuclear Methods in Environmental Res., J. R. Vogt and W. Meyer, Ed., U. of Missouri, Columbia, MO (1974).
39. J. Heron, Determination of Phosphate in Water After Storage in Polyethylene, Limnol. Oceanogr., 7, 316-321 (1962).
40. F. J. Philbert, The Effect of Sample Preservation by Freezing Prior to Chemical Analysis of Great Lake Waters, Proc. 16th Conf. Great Lakes Res., 282-293, International Association Great Lakes Res. (1973).
41. E. C. Kuehner and D. H. Freeman, Containers for Pure Substances, 297-306, in Purification of Inorganic and Organic Materials, M. Zief, Ed., Marcel Dekker, New York, NY (1969).
42. M. H. Bothner and D. E. Robertson, Mercury Contamination of Sea Water Samples Stored in Polyethylene Containers, Anal. Chem., 47, 592-595 (1975).

43. J. Moody, T. Rains, and M. Epstein (private communication).
44. B. A. Malo and R. A. Baker, Cationic Concentration by Freezing, in Trace Inorganics in Water, Advances in Chemistry, Series 73, 149-163, Ed., R. F. Gould, American Chemical Society, Washington, DC (1968).
45. K. K. S. Pillay, C. C. Thomas, Jr., J. A. Sondel, and C. M. Hyche, Determination of Mercury in Biological and Environmental Materials by Neutron Activation Analysis, Anal. Chem., 43, 1419-1425 (1971).
46. P. D. LaFleur, Retention of Mercury When Freeze-Drying Biological Materials, Anal. Chem., 45, 1534-1536 (1973).
47. J. S. Hislop and A. Parker, The Use of a Laser for Cutting Bone Samples Prior to Chemical Analysis, Analyst, 98, 694 (1973).
48. J. R. Montgomery, S. E. Kolehmainen, M. D. Banus, B. J. Bendien, J. L. Donaldson, and J. A. Ramirez, Individual Variation of Trace Metal Content in Fish, NBS, TS.*
49. J. Versieck, A. Speecke, J. Hoste, and F. Barbier, Trace Contamination in Biopsies of the Liver, Clin. Chem., 19, 472-475 (1973).
50. G. L. Fisher, L. G. Davies, and L. S. Rosenblatt, The Effects of Container Composition, Storage Duration, and Temperature on Serum Mineral Levels, NBS, TS.*
51. W. G. Walter, R. A. McBee, and K. L. Temple, Introduction to Microbiology, D. Van Nostrand Co., NY (1973).
52. F. A. Ibbott, Sampling for Clinical Chemistry, NBS, TS.*
53. S. H. Omang and O. D. Vellar, Concentration Gradients in Biological Samples During Storage, Freezing and Thawing, Z. Anal. Chem., 269, 177-181 (1974).
54. V. T. Bowen and D. Sutton, Comparative Studies of Mineral Constituents of Marine Sponges, Journal of Marine Research, 10, 153-167 (1951).
55. R. H. Gibbs, Jr., E. Jarosewich, and H. L. Windom, Heavy Metal Concentrations in Museum Fish Specimens: Effects of Preservatives and Time, Science, 184, 475-477 (1974).

56. A. Cockburn, R. A. Barraco, T. A. Reymann, and W. H. Peck, Autopsy of an Egyptian Mummy, *Science*, 187, 1155-1160 (1975).
57. R. G. Smith, Department of Environmental and Industrial Health, University of Michigan, Ann Arbor, MI.
58. R. A. Kehoe, *J. Res. Publ. Health Hyg.*, 24, 1 (1961).
59. L. J. Goldwater, *Mercury: A History of Quicksilver*, York, Baltimore (1972).
60. O. J. Attoe, Potassium Fixation and Release in Soils Occurring Under Moist and Drying Conditions, *Soil Sci. Soc. Proc.*, 11, 145-149 (1946).
61. E. B. Schalscha, C. Gonzalez, I. Vergara, G. Galindo, and A. Schatz, Effect of Drying on Volcanic Ash Soils in Chile, *Soil Sci. Soc. Proc.*, 29, 481-482 (1965).
62. N. J. Barrow, Studies on the Mineralization of Sulphur from Soil Organic Matter, *Aust. J. Agric. Res.*, 12, 306-319 (1961).
63. M. I. Harpstead and B. L. Brage, Storage of Soil Samples and Its Effect on the Subsequent Accumulation of Nitrate Nitrogen During Controlled Incubation, *Proc. Soil Sci. Soc. Am.*, 22, 326-328 (1958).
64. H. F. Birch, The Effect of Soil Drying on Humus Decomposition and Nitrogen Availability, *Plant and Soil*, 10, 9-30 (1958).
65. H. F. Birch, Further Observations on Humus, Decomposition and Nitrification, *Plant and Soil*, 11, 262-286 (1959).
66. H. F. Birch, Nitrification in Soils After Different Periods of Dryness, *Plant and Soil*, 12, 81-96 (1960).
67. Z. Nevo and J. Hagin, Changes Occurring in Soil Samples During Air-Dry Storage, *Soil Science*, 102, 157-160 (1966).
68. P. R. Hesse, p. 12 in *A Textbook of Soil Chemical Analysis*, John Murray Publishers, Ltd., London (1971).
69. T. H. Arkely, D. N. Munns, and C. M. Johnson, Preparation of Plant Tissues for Micronutrient Analysis: Removal of Dust and Spray Contaminants, *J. Agric. Food Chem.*, 8, 318-321 (1960).

70. J. V. Lagerwerff, Uptake of Cadmium, Lead, and Zinc by Radish from Soil and Air, *Soil Sci.*, 111, 129-133 (1971).
71. D. E. Koeppe and R. J. Miller, p. 207 in *Environmental Pollution by Lead and Other Metals*, Progress Rept. to NSF-RANN, May 1971 - April 1972, Univ. of Illinois.
72. H. E. Bruce and S. P. Cram, Sampling Marine Organisms and Sediments for High Precision Gas Chromatographic Analysis of Aromatic Hydrocarbons, pp. 181-182 in *Marine Pollution Monitoring*, Proc. of a Workshop held at NBS, Gaithersburg, MD, NBS Spec. Publ. 409 (1974).
73. Federal Working Group on Pest Management, Guidelines on Sampling and Statistical Methodologies for Ambient Pesticide Monitoring, Washington, DC (1974).
- 73a. Ibid. (1975).
74. W. H. Lawrence, J. L. Mitchell, W. L. Guess, and J. Autian, Toxicity of Plastics Used in Medical Practice-I, *J. Pharm. Sciences*, 52, 958-963 (1963).
75. J. Autian and A. J. Kapadia, The Leaching of a Constituent from Medical-Grade Plastic Tubings, *Drug Std.*, 28, 101-103 (1960).
76. G. W. Gibbs, Asbestos Contamination by Storage in Polyethylene Bags, a report which is included in a paper accepted for publication by the American Industrial Hygiene Assoc. Journal.
77. A. J. Bauman, R. E. Cameron, G. Kritchevsky, and G. Rouser, Detection of Phthalate Esters as Contaminants of Lipid Extracts from Soil Samples Stored in Standard Soil Bags, *Lipids*, 2, 85-86 (1967).
78. D. F. Goerlitz and E. Brown, Methods for the Analysis of Organic Substances in Water, in *Techniques of Water-Resources Investigations*, USGS Cat. #19:15/5: Bk 5, Chap. A3 (1972).
79. C. S. Giam and H. S. Chan, Control of Blanks in the Analysis of Phthalates in Air and Ocean Samples, NBS, TS.*
80. C. S. Giam, H. S. Chan, and G. S. Neff, Sensitive Method for Determination of Phthalate Ester Plasticizers in Open-Ocean Biota Samples, *Anal. Chem.*, 47, 2225-2229 (1975).

81. H. S. Hertz, S. N. Chesler, W. E. May, B. H. Gump, D. P. Enagonio, and S. P. Cram, Methods for Trace Organic Analysis in Sediments and Marine Organisms, pp. 197-199 in Marine Pollution Monitoring, Proc. of a Workshop held at NBS, Gaithersburg, MD, NBS Spec. Publ. 409 (1974).
82. P. B. Hamilton and T. T. Myoda, Contamination of Distilled Water, HCl, and NH₄OH with Amino Acids, Proteins, and Bacteria, Clin. Chem., 20, 687-691 (1974).
83. M. S. Favero, L. A. Carson, W. W. Bond, and N. J. Peterson, Pseudomonas aeruginosa: Growth in Distilled Water from Hospitals, Science, 173, 836--838 (1971).
84. Y. Wolman and S. L. Miller, Amino Acid Contamination of Aqueous Hydrochloric Acid, Nature, 234, 548-549 (1971).
85. B. E. Conway, H. Angerstein-Kozłowska, W. B. A. Sharp, and E. E. Criddle, Ultrapurification of Water for Electrochemical and Surface Chemical Work by Catalytic Pyrodistillation, Anal. Chem., 45, 1331-1336 (1973).
86. D. Straughan, Field Sampling Methods and Techniques for Marine Organisms and Sediments, Marine Pollution Monitoring, Proc. of a Workshop held at NBS, Gaithersburg, MD, NBS Spec. Publ. 409 (1974).
87. D. J. Jeffries and C. H. Walker, Uptake of pp'-DDT and its Post-Mortem Breakdown in the Avian Liver, Nature, 212, 533-534 (1966).
88. M. C. French and D. J. Jeffries, The Preservation of Biological Tissue for Organochlorine Insecticide Analysis, Bull. of Environ. Contam. and Tox., 6, 460-463 (1971).
89. D. Bristol, Effects of Storage Conditions on Residues of 2,4-D and 2,4-DCP in Potatoes, NBS, TS.*
90. M. E. Zabik and L. Dugan, Jr., Potential of Freeze Drying for Removal of Chlorinated Hydrocarbon Insecticides from Eggs, Jour. Food Sci., 36, 87-88 (1971).
- 90a. Robert J. Morris, The Preservation of Some Oceanic Animals for Lipid Analyses, J. Fish. Res. Board Canada, 29, 1303-1307 (1972).
91. D. Smith, Influence of Drying and Storage Conditions on Nonstructural Carbohydrate Analysis of Herbage Tissue - A Review, J. Br. Grassld. Soc., 28, 129-134 (1973).

92. L. F. Molloy, D. J. Giltrap, T. W. Collie, and A. J. Metson, Degradation of Higher Fatty Acids in Perennial Rye Grass and White Clover Following Drying and Storage, *J. Sci. Food and Agric.*, 25, 595-606 (1974).
93. W. P. Iverson, Private Communication.
94. S. Fleischer and M. Kervina, Long-Term Preservation of Liver for Subcellular Fractionation, *Methods in Enzymology*, 31, Pt. A, 3-6 (1974).
- 94a. D. W. McPeak and F. R. Camp, Jr., Frozen Blood Shipping, *Military Medicine*, 140, 468-470 (1975).
95. C. R. Valeri, A. H. Runck, and L. E. McCallum, Observations on Autologous, Previously Frozen, Deglycerolyzed, Agglomerated Resuspended Red Cells. I. Effect of Storage Temperatures. II. Effect of Adenine Supplementation of Glycerolized Red Cells Prior to Freezing, Transfusion, 7, 105-116 (1967).
96. H. T. Meryman and M. Hornblower, A Method for Freezing and Washing Red Blood Cells Using a High Glycerol Concentration, *Transfusion*, 12, 145-156 (1972).
97. J. G. Gibson, J. L. Tullis, R. J. Tinch, W. R. Ryan, and S. Diforte, The Post-Thaw Viability of ACD and CPD Blood Preserved in the Frozen State With and Without Added Adenine, *Transfusion*, 12, 198-207 (1972).
98. J. Farrant, S. C. Knight, L. E. McGann, J. O'Brien, Optimal Recovery of Lymphocytes and Tissue Culture Cells Following Rapid Cooling, *Nature*, 249, 452-453 (1974).

* Symposium on Accuracy in Trace Analysis: Sampling, Sample Handling, and Analysis, Proc. of the 7th IMR Symp., P. D. LaFleur, Ed., NBS Special Publ. 422 (in press, 1975).

Bibliography Addendum A - Microbiologicals

- A-1 W. M. Abbott and J. S. Hembree, Absence of Antigenicity in Freeze-Dried Skin Allografts, Cryobiol., 6, 416-418 (1970).
- A-2 M. D. Alur and N. Grecz, Mechanism of Injury of Escherichia coli by Freezing and Thawing, Biochem. and Biophys. Res. Commun., 62, 308-312 (1975).
- A-3 H. Bank, Freezing Injury in Tissue Cultured Cells as Visualized by Freeze-Etching, Exptl. Cell Res., 85, 367-376 (1974).
- A-4 J. B. Bateman, P. A. McCaffrey, R. J. O'Connor, and G. W. Monk, Relative Humidity and the Killing of Bacteria, Appl. Microbiol., 6, 567-571 (1961).
- A-5 S. Berman, P. L. Altieri, A. Groffinger, and J. P. Lowenthal, Freeze Drying Various Attenuated Strains of Pasteurella Pestis, Cryobiol., 7, 40-43 (1970).
- A-6 S. Berman, P. L. Altieri, A. Groffinger, J. P. Lowenthal, and S. B. Formal, Freeze Drying Various Strains of Shigella, Appl. Microbiol., 16, 1779-1781 (1968).
- A-7 H. L. Braid, R. F. Hagerty, and W. H. Lee, Jr., Preservation of Cellular Viability of Human Cartilage at Low Temperature, Transpl., 4, 94-99 (1966).
- A-8 B. L. Brown, S. C. Nagle, Jr., J. D. Lehmann, and C. D. Rapp, Preservation of Insect Cells in Liquid Nitrogen, Tech. Manuscript 590, Dept. of the Army, Fort Detrick, Frederick, MD (1970).
- A-9 B. L. Brown, S. C. Nagle, Jr., J. D. Lehmann, and C. D. Rapp, Storage of Aedes Aegypti and Aedes Albopictus Cells Under Liquid Nitrogen, Cryobiol., 7, 249-251 (1971).
- A-10 M. S. Brown and F. W. Reuter, Freezing of Nonwoody Plant Tissues. III. Videotape Micrography and the Correlation between Individual Cellular Freezing Events and Temperature Changes in the Surrounding Tissue, Cryobiol., 11, 185-191 (1974).
- A-11 W. Brüschweller and W. Gehring, A Method for Freezing Living Ovaries of Drosophila melanogaster Larvae and Its Application to the Storage of Mutant Stocks, Separatum Experientia, 29, 135 (1973).

- A-12 W. A. Cassel and K. M. McCaskill, Ehrlich Ascites Tumor Preservation for 15 Years - A Simple Method, Appl. Microbiol., 28, 726 (1974).
- A-13 W. H. J. Crombach, Deep-Freezing of Bacterial DNA for Thermal Denaturation and Hybridization Experiments, J. Microbiol. and Serology, 39, 249-255 (1973).
- A-14 R. Digirolamo, J. Liston, and J. Matches, The Effects of Freezing on the Survival of Salmonella and E. coli in Pacific Oysters, J. Food Sci., 35, 13-16 (1970).
- A-15 J. Farrant, Mechanism of Cell Damage During Freezing and Thawing and its Prevention, Nature, 205, 1284-1287 (1965).
- A-16 J. Farrant, S. Knight, L. E. McGann, J. O'Brien, Optimal Recovery of Lymphocytes and Tissue Cells Following Rapid Cooling, Nature, 249, 452-453 (1974).
- A-17 W. N. Fishbein, Mechanism of Freezing Damage to Mouse Liver Using a Mitochondrial Enzyme Assay. III. Cryophyllaxis with DMSO and Enzyme Localization, Cryobiol., 8, 293-299 (1971).
- A-18 W. N. Fishbein and R. E. Stowell, Studies of the Mechanism of Freezing Damage to Mouse Liver Using a Mitochondrial Enzyme Assay, I. Temporal Localization of the Injury Phase During Slow Freezing, Cryobiol., 4, 283-289 (1968).
- A-19 Ibid, II. Comparison of Slow and Rapid Cooling Rates, 6, 227-234 (1969).
- A-20 M. P. Garber and P. L. Steponkus, Alterations in Chloroplast Membranes during Cold Acclimation and Freezing, Cryobiol., 10, 532 (1973).
- A-21 L. J. Goatcher, S. E. Engler, D. C. Wagner, and D. C. Westhoff, Effect of Storage at 5°C on Survival of Vibrio Parahaemolyticus in Processed Maryland Oysters, J. Milk Food Tech., 37, 74-77 (1974).
- A-22 R. Gomez, M. Takano, and A. J. Sinskey, Characteristics of Freeze-Dried Cells, Cryobiol., 10, 368-374 (1973).
- A-23 E. Griffiths and H. F. Birch, Microbiological Changes in Freshly Moistened Soil, Nature, 189, 424 (1961).

- A-24 D. F. Hiltz, L. J. Bishop, and W. J. Dyer, Accelerated Nucleotide Degradation and Glycolysis During Warming to and Subsequent Storage at -5°C of Prerigor, Quick-Frozen Adductor Muscle of the Sea Scallop (Placopecten magillanicus), J. Fish Res. Board of Canada, 31, 1181-1187 (1974).
- A-25 International Atomic Energy Agency, Reference Methods for Marine Radioactivity Studies, Tech. Rept. Series 118, IAEA, Vienna, pp. 26, 28 (1970).
- A-26 E. Israeli and A. Kohn, Protection of Lyophilized E. coli by Colicin El Treatment, FEBS Letters, 26, 323-326 (1972).
- A-27 E. Israeli, A. Kohn, and J. Gitelman, The Molecular Nature of Damage by Oxygen to Freeze-Dried Escherichia coli, Cryobiol., 12, 15-25 (1975).
- A-28 D. W. Janssen and F. F. Busta, Influence of Milk Components on the Injury, Repair of Injury and Death of Salmonella anatum Cells Subjected to Freezing and Thawing, Appl. Microbiol., 26, 725-732 (1973).
- A-29 B. Kirsop, The Stability of Biochemical, Morphological and Brewing Properties of Yeast Cultures Maintained by Subculturing and Freeze-Drying, J. Inst. of Brew. (London), 80, 565-570 (1974).
- A-30 M. Kuzminska, A. Szdlowski, I. Werner, and L. Obrzut, Microbiological Analysis of Fish Dishes During Freezing and Subsequent Cold Storage at -22°C, International Institute of Refrigeration, 1972, 123-132.
- A-31 K. A. Lehner, Freezing Preservation of Foods with Carbon Dioxide and Dry Ice, Amer. Soc. Heat. Refrig. Air Cond. Eng. J., 13, 41-43 (1971).
- A-32 J. Lundy and W. G. Fitz-William, A Portable Dry-Ice Storage Chamber for Enhanced Preservation of Enzymes in Frozen Tissue Specimens, Stain Tech., 46, 259-261 (1971).
- A-33 G. M. Martin, A Case for Regional Culture Collections of Microorganisms, Nature, 247, 431-433 (1974).
- A-34 T. Matsushashi, Studies on Freezing and Drying of Agar Gel, Refrig., 49, 966-973 (1974).

- A-35 D. E. McComb and C. I. Puzniak, Micro Cell Culture Method for Isolation of Chlamydia trachomatis, Appl. Microbiol., 28, 727-729 (1974).
- A-36 J. Nath and J. O. Anderson, Some Biochemical Alterations Associated with the Freeze Preservation of Pollen, Cryobiol., 10, 533 (1973).
- A-37 O. Novick, E. Israeli, and A. Kohn, Nucleic Acid and Protein Synthesis in Reconstituted Lyophilized Escherichia coli Exposed to Air, J. Appl. Bact., 35, 185-191 (1972).
- A-38 K. Ostrowski, Current Problems of Tissue Banking, Transpl. Proc., 1, 126-131 (1969).
- A-39 W. Partmann, Some Effects of Defined Conditions of Freezing and Thawing on Histological Changes in White Muscle of Carp, International Inst. of Refrig., 1972, 77-84.
- A-40 F. F. G. Rommerts, L. G. van Doorn, H. Galjaard, B. A. Cook, and H. J. van der Molen, Dissection of Wet Tissue and of Freeze-Dried Sections in the Investigation of Seminiferous Tubules and Interstitial Tissue from Rat Testis, J. Histochem. and Cytochem., 21, 572-579 (1973).
- A-41 V. U. Schneider, J. Hahn, and H. Sulzer, Preliminary Results of Low Temperature Preservation in Mouse and Rabbit Ova, Dtsch. Tierarztl. Wschr., 81, 470-472 (1974).
- A-42 T. H. Scholten and J. Yang, Evaluation of Unpreserved and Preserved Stools for the Detection and Identification of Parasites, Amer. J. of Clin. Path., 62, 563-567 (1974).
- A-43 K. W. Sell, Viability Assay of Organized Tissues and Organs, Cryobiol., 4, 133-135 (1967).
- A-44 E. M. Simon and M. V. Schneller, The Preservation of Ciliated Protozoa at Low Temperature, Cryobiol., 10, 421-426 (1973).
- A-45 R. B. Smittle, S. E. Gilliland, and M. L. Speck, Death of Lactobacillus bulgaricus Resulting from Liquid Nitrogen Freezing, Appl. Microbiol., 24, 551-554 (1972).
- A-46 J. Stadhouwers, G. Hup, and L. A. Jansen, A Study of the Optimum Conditions of Freezing and Storing Concentrated Mesophilic Starters, Neth. Milk Dairy J., 25, 229-239 (1971).

- A-47 P. L. Steponkus and S. C. Wiest, Freezing Injury of Plant Plasma Membranes, *Cryobiol.*, 10, 532 (1973).
- A-48 M. Suzuki, Stability and Residual Moisture Content of Dried Vaccinia Virus, *Cryobiol.*, 10, 432-434 (1973).
- A-49 Ibid. Protectants in the Freeze-Drying and the Preservation of Vaccinia Virus, 435-439.
- A-50 M. Takano, J. Sado, T. Ogawa, and G. Terui, Freezing and Drying of Spirulina platensis, *Cryobiol.*, 10, 440-444 (1973).
- A-51 R. Todorova, On the Lyophilization of Viruses and Virus Vaccines, *Vet. Med. Nauki, Sofia*, 10, 52-53, (1973).
- A-52 L. E. Towill, P. Mazur, and G. P. Howland, Plasmolysis Injury as a Factor in Freezing Injury in Plant Tissue Culture, *Cryobiol.*, 10, 532 (1973).
- A-53 S. Tsuru, Preservation of Marine and Fresh Water Algae by Means of Freezing and Freeze Drying, *Cryobiol.*, 10, 445-452 (1973).
- A-54 S. Tsuru, Protection Mechanisms of Biological Materials During Freezing and Thawing, (Fermentation Research Institute, Agency of Industrial Science and Technology), 97-102, I.I.F.-I.I.R.-Commission CI-Sappors, 1973-5.
- A-55 K. J. Whittle, A Multiple Sampling Technique for Use with the Cell-Fragility Method of Determining Deteriorative Changes in Frozen Fish, *J. Sci. Fd. Agric.*, 24, 1383-1389 (1973).
- A-56 G. L. Zink and H. C. Hines, The Freezing and Preservation of Bovine Erythrocytes in Liquid Nitrogen, *Anim. Blood Grps. biochem. Genet.*, 1, 23-32 (1970).

Bibliography Addendum B - Blood

- B-1 J. Abramowitz, A. Stracher, and T. C. Detwiler, Proteolysis of Myosin during Platelet Storage, *J. Clin. Investig.*, 53, 1493-1496 (1974).
- B-2 O. Åkerblom and C. F. Högman, Frozen Blood: A Method for Low-Glycerol, Liquid Nitrogen Freezing Allowing Different Post-Thaw Deglycerolization Procedures, *Transf.*, 14, 16-26 (1974).
- B-3 H. Chaplin, Jr., E. Beutler, J. A. Collins, E. R. Giblett, and H. F. Polesky, Current Status of Red-Cell Preservation and Availability in Relation to the Developing National Blood Policy, *New Eng. J. Med.*, 291, 68-74 (1974).
- B-4 D. G. Corby, K. A. Preston, and T. P. O'Barr, Adverse Effect of Gel Filtration on the Function of Human Platelets, *Proc. Soc. Exptl. Biol. and Med.*, 146, 96-98 (1974).
- B-5 J. P. Crowley, E. M. Skrabut, and C. R. Valeri, Immunocompetent Lymphocytes in Previously Frozen Washed Red Cells, *Vox Sang.*, 26, 513-517 (1974).
- B-6 E. Dobry, J. Fiala, and J. Livora, A Comparison of the Cryoprotective Effect of Glycerol and Dimethyl Sulfoxide in the Preservation of Murine Bone Marrow, *Blut Zeitschr. Gesamte Blut.*, 23, 359-362 (1971).
- B-7 J. R. Geraci and F. R. Engelhardt, The Effects of Storage Time, Temperature, and Anticoagulants on Harp Seal, *Phoca Groenlandica* Hemograms: A Simulated Field Study, *Physiol. Zool.*, 47, 22-28 (1974).
- B-8 M. Hills, G. I. C. Ingram, and M. O. Matchett, Lyophilized Plasma as an Assay Standard for Factor VIII: Calibration and Control with Fresh Plasma Samples, *Brit. J. Haemat.*, 18, 617-624 (1970).
- B-9 M. S. Jacobson, R. Parkman, L. N. Button, R. J. Jaeger, and S. V. Kevy, The Toxicity of Human Serum Stored in Flexible Polyvinyl Chloride Containers on Human Fibroblast Cell Cultures: An Effect of Di-2-Ethylhexyl Phthalate, *Res. Commun. Chem. Path. and Pharmacol.*, 9, 315-323 (1974).

- B-10 S. M. Lewis and C. T. H. Stoddart, Effects of Anti-coagulents and Containers (Glass and Plastic) on the Blood Count, *Lab. Prac.*, 20, 787-792 (1971).
- B-11 S. Murphy, S. N. Sayar, N. L. Abdou, and F. H. Gardner, Platelet Preservation by Freezing. Use of Dimethylsulfoxide as Cryoprotective Agent, *Transf.*, 14, 139-144 (1974).
- B-12 J. Niedworok, Comparative Investigations of Plasma Lipids during the Blood Preservation at Ultra-Low Temperatures in Relation to the Preservative, *Acta Haemat. Pol.*, 2, 172-173 (1971).
- B-13 V. S. Seidl, Tiefkühlkonservierung von Blut, *Blut Zeitschr. Gesamte Blut.*, 25, 145-149 (1972).
- B-14 L. Weatherbee, H. H. Spencer, C. T. Knorpp, S. M. Lindenauer, P. W. Gikas, and N. W. Thompson, Coagulation Studies after Transfusion of Hydroxyethyl Starch Protected Frozen Blood in Primates, *Transf.*, 14, 109-115 (1974).
- B-15 F. C. Wessling and P. L. Blackshear, The Effect of Gases on the Recovery of Human Red Blood Cells, *Cryobiol.*, 7, 265-273 (1971).
- B-16 A. E. Woolgar, Hemolysis of Human Red Blood Cells by Freezing and Thawing in Solutions Containing Polyvinylpyrrolidone: Relationship with Posthypertonic Hemolysis and Solute Movements, *Cryobiol.*, 11, 52-59 (1974).

Bibliography Addendum C - Biological Sample
Preparation and Storage

- C-1 A. Abu-Samra, J. S. Morris, and S. R. Koirtyohann, Wet Ashing of Some Biological Samples in a Microwave Oven, *Anal. Chem.*, 47, 1475-1477 (1975).
- C-2 D. Behne and P. A. Matamba, Drying and Ashing of Biological Samples in the Trace Element Determination by Neutron Activation Analysis, *Z. Anal. Chem.*, 274, 195-197 (1975).
- C-3 F. R. Camp, F. R. Ellis, C. E. Shields, and M. M. Werline Long-Term Preservation of Biologicals for the Forensic Laboratory and Their Areas of Application, *J. Forensic Sci.*, 13, 419-432 (1968).
- C-4 J. Chirife and M. Karel, Contribution of Adsorption to Volatile Retention in a Freeze-Dried Food Model Containing PVP, *J. Food Science*, 38, 768-771 (1973).
- C-5 J. Chirife and M. Karel, Volatile Retention During Freeze Drying of Protein Solutions, *Cryobiol.*, 11, 107-115 (1974).
- C-6 I. Y. Donev, Rapid Homogenization and Drying of Biological Material, in *Accuracy in Trace Analysis: Sampling, Sample Handling, and Analysis*, Proc. of the 7th IMR Symp., P. D. LaFleur, Ed., NBS Spec. Publ. 422 (in press 1975).
- C-7 N. El Bassam and F. Mertens, Influence of Various Storage and Drying Methods on the Chemical Composition of Sludge, *Landbauforsch. Voelkenrode*, 22, 41-44 (1972).
- C-8 J. Flink and M. Karel, Effects of Process Variables on Retention of Volatiles in Freeze-Drying, *J. Food Sci.*, 35, 444-447 (1970).
- C-9 J. M. Flink and T. P. Labuza, Retention of 2-Propanol at Low Concentration by Freeze-Drying Carbohydrate Solutions, *J. Food Sci.*, 37, 617-618 (1972).
- C-10 R. Gomez, M. Takano, and A. J. Sinskey, Characteristics of Freeze-Dried Cells, *Cryobiology*, 10, 368-374 (1973).
- C-11 T. T. Gorsuch, Dissolution of Organic Materials, in *Accuracy in Trace Analysis: Sampling, Sample Handling, and Analysis*, Proc. of the 7th Symp., P. D. LaFleur, Ed., NBS Spec. Publ. 422 (in press 1975).

- C-12 T. T. Gorsuch, The Destruction of Organic Matter, Pergamon Press, Oxford, New York, Toronto, Sydney (1970).
- C-13 G. J. Haas, S. Barnett, and H. E. Prescott, Jr., Pressure-Freezing -- A New Pretreatment Process to Prevent Shrivelling during Drying of Cellular Foods, in part in *Cryobiol.*, 9, 101-106 (1972) and in part in *J. Food Sci.*, 37 (1972).
- C-14 R. Hamm, K. Potthast, and L. Acker, Influence of Water Activity on Enzymatic Changes in Freeze-Dehydrated Muscle. I. The Breakdown of Adenosine Triphosphate, *Z. Lebensm. Unters.-Forsch.*, 154, 73-79 (1974).
- C-15 J. A. Hesek and R. C. Wilson, Use of Microwave Oven in In-Process Control, *Anal. Chem.*, 46, 1160 (1974).
- C-16 C. S. Huber, R. B. Harrington, and W. J. Stadelman, Effect of Freezing Rate and Freeze-Drying on the Soluble Proteins of Muscle. II. Turkey Muscle, *J. Food Sci.*, 35, 233-236 (1970).
- C-17 C. S. Huber and W. J. Stadelman, Effect of Freezing Rate and Freeze-Drying on the Soluble Proteins of Muscle. I. Chicken Muscle, *J. of Food Sci.*, 35, 229-232 (1970).
- C-18 B. M. Kilcullen and R. D. Harter, A Simple System for Freeze Drying, *J. Chem. Ed.*, 51, 590 (1974).
- C-19 B. J. Longan, G. A. Hruzek, and E. E. Burns, Effect of Processing Variables on Volatile Retention of Freeze-Dried Carrots, *J. Food Science*, 39, 1191-1194 (1974).
- C-20 H. A. Massaldi and C. J. King, Volatiles Retention During Freeze-Drying of Synthetic Emulsion, *J. Food Sci.*, 39, 438-444 (1974).
- C-21 J. Parker and H. M. Smith, Design and Construction of a Freeze Dryer Incorporating Improved Standards of Biological Safety, *J. Appl. Chem. Biotechnol.*, 22, 925-932 (1972).
- C-22 H. Souzu, The Phospholipid Degradation and Cellular Death Caused by Freeze-Thawing or Freeze-Drying of Yeast, *Cryobiol.*, 10, 427-431 (1973).
- C-23 L. U. Thompson and O. Fennema, Effect of Freezing on Oxidation of L-Ascorbic Acid, *J. Agric. Food Chem.*, 19, 121-124 (1971).

- C-24 J. M. Tuomy, Freeze-Drying of Foods for the Armed Services, Tech. Rept. 72-28-FL, U. S. Army Natick Lab., Natick, Mass. (1971).
- C-25 V. L. Voznesenskii and L. A. Filippova, Instrument for Freeze-Drying Tissues, Soviet Plant Physiol., 16, 793-794 (1969).
- C-26 J. W. Young and G. D. Christian, Simple Inexpensive Freeze-Drying Procedure, Anal. Chem., 45, 1296 (1973).

Acknowledgment

This work was supported in part by the Environmental Protection Agency under the Interagency Agreement No. EPA-1AG-D5-0568.


Note:

Certain Trade names and company names are used in this paper. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards.

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET		1. PUBLICATION OR REPORT NO. <i>NBS TN-929</i>	2. Gov't Accession No.	3. Recipient's Accession No.
4. TITLE AND SUBTITLE A Survey of Current Literature on Sampling, Sample Handling, and Long Term Storage for Environmental Materials			5. Publication Date October 1976	
			6. Performing Organization Code	
7. AUTHOR(S) E. J. Maienthal and D. A. Becker			8. Performing Organ. Report No.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE WASHINGTON, D.C. 20234			10. Project/Task/Work Unit No.	
			11. Contract/Grant No.	
12. Sponsoring Organization Name and Complete Address (Street, City, State, ZIP) Same as 9.			13. Type of Report & Period Covered Final	
			14. Sponsoring Agency Code	
15. SUPPLEMENTARY NOTES To be submitted to Analytical Chemistry				
16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.) This article is the result of an extensive literature survey to establish optimum sampling, sample handling and long term storage techniques for a wide variety of environmental samples. to retain sample integrity. The components of interest in these samples are trace elements, organics, pesticides, radionuclides or microbiologicals. This survey was done both manually and by use of various bibliographical retrieval services. Also the advice and opinions of workers in various aspects of the fields was obtained.				
17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons) Environmental samples; Long-term storage; Microbiologicals; Organics; Pesticides; Sample handling; Sampling; Chemical analysis; Radionuclides; Trace Elements				
18. AVAILABILITY <input type="checkbox"/> Unlimited <input type="checkbox"/> For Official Distribution. Do Not Release to NTIS <input checked="" type="checkbox"/> Order From Sup. of Doc., U.S. Government Printing Office Washington, D.C. 20402, SD Cat. No. C13 .46:929 <input type="checkbox"/> Order From National Technical Information Service (NTIS) Springfield, Virginia 22151		19. SECURITY CLASS (THIS REPORT) UNCLASSIFIED		21. NO. OF PAGES 40
		20. SECURITY CLASS (THIS PAGE) UNCLASSIFIED		22. Price \$0.85

get
a line on
science and
technology.
subscribe to

DIMENSIONS



Whether you're in business, or a teacher, scientist, or consumer, you'll want to keep up with the latest developments in science and technology. DIMENSIONS/NBS, the monthly magazine from the Commerce Department's National Bureau of Standards, can help keep you informed. Every day at NBS, one of the nation's largest research laboratories, scientists seek new answers to a host of national problems, including energy conservation, product safety, metric conversion, and pollution abatement. Their findings, reported each month in DIMENSIONS/NBS, have a direct impact on our daily lives.

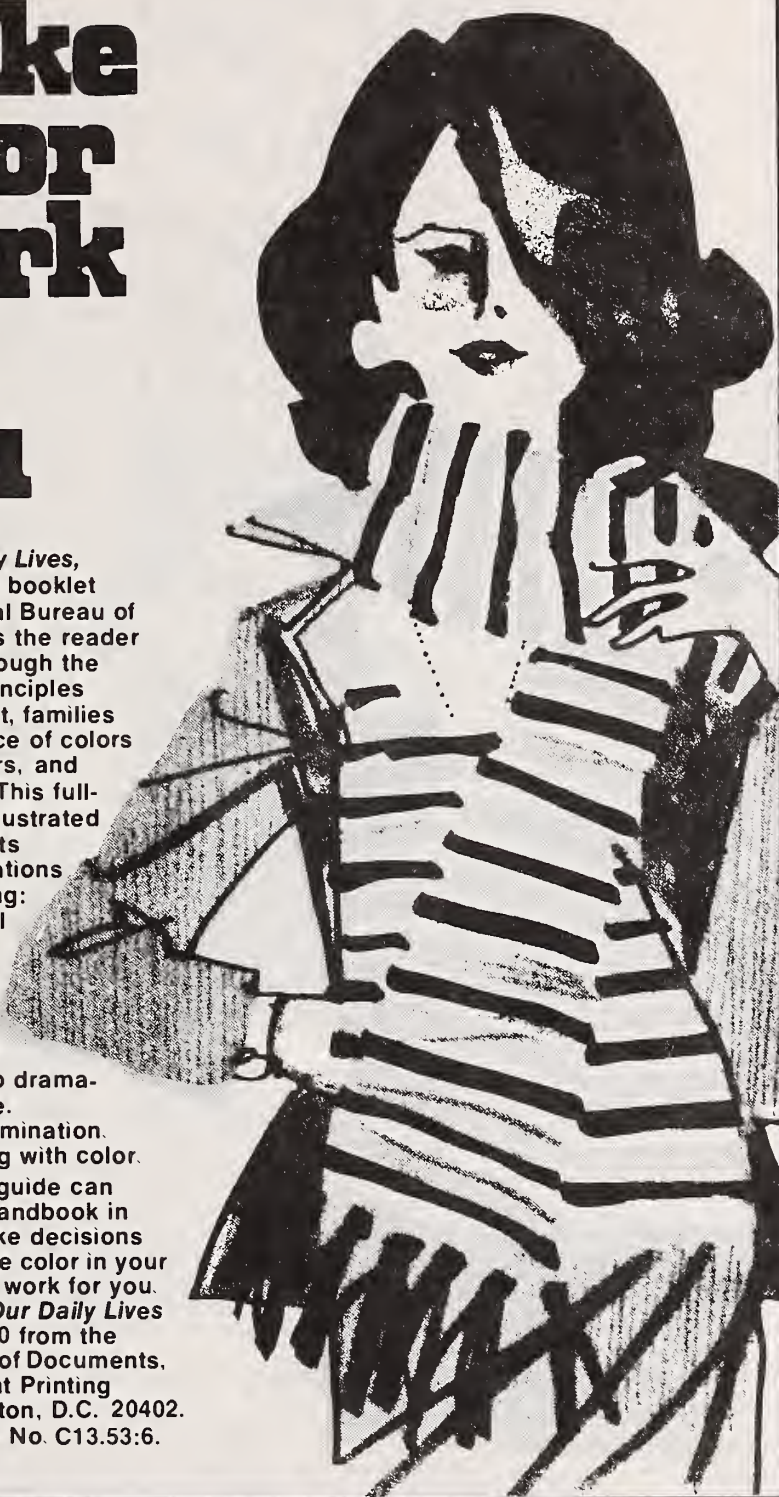
Subscription price: \$9.45 per year.
Order prepaid from the
Superintendent of Documents,
U.S. Government Printing Office,
Washington, D.C. 20402
SD Catalog No. C13.13

make color work for you

Color in our Daily Lives, a new consumer booklet from the National Bureau of Standards, takes the reader step by step through the fundamental principles of color and light, families of color, influence of colors upon other colors, and color harmony. This full-color, 32-page illustrated booklet highlights practical applications of color, including:

- Your personal color plan.
- Your color environment.
- Color plans for the home.
- Using color to dramatize or to hide.
- Color and illumination.
- Experimenting with color.

This new basic guide can serve as your handbook in helping you make decisions about how to use color in your life and make it work for you. Order *Color in Our Daily Lives* prepaid for \$1.70 from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. Use SD Catalog No. C13.53:6.



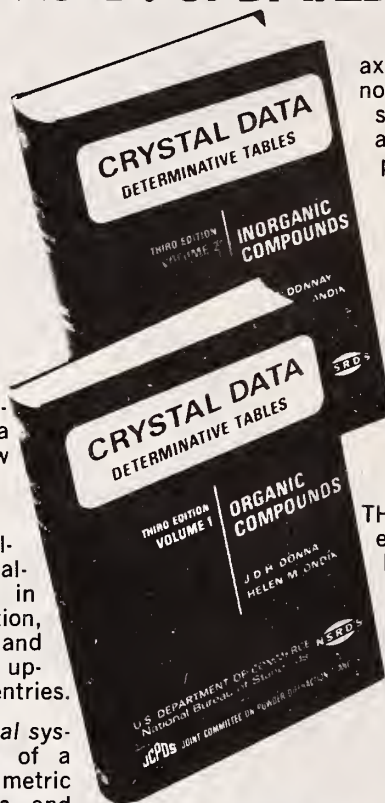
SINGLE CRYSTAL DATA

REVISED! UPDATED!

In 1954, the first edition of CRYSTAL DATA (Determinative Tables and Systematic Tables) was published as Memoir 60 of the Geological Society of America. In 1960, the second edition of the Determinative Tables was issued as Monograph 5 of the American Crystallographic Association, and in 1967, the Systematic Tables were issued as Monograph 6. These editions proved extremely valuable to crystallographers throughout the world. Recognizing the need for updated crystallographic information, the National Bureau of Standards Office of Standard Reference Data has sponsored the issuance of a new edition.

This, the THIRD EDITION, should be of particular interest not only to crystallographers but also to chemists, mineralogists, physicists and individuals in related fields of study. The current edition, which comprises two volumes, Organic and Inorganic, is a thoroughly revised and updated work, containing over 25,000 entries.

The entries are listed, *within each crystal system*, according to increasing values of a determinative number: a/b ratio in trimetric systems, c/a ratio in dimetric systems, and cubic cell edge a , in the isometric system. In addition, the following information is given:



INORGANIC VOLUME \$50.00

ORGANIC VOLUME \$30.00

Plus shipping and handling

axial ratio(s) and interaxial angles not fixed by symmetry, cell dimensions, space group or diffraction aspect, number of formula units per unit cell, crystal structure, (whether determined), measured density and x-ray calculated density. Also listed is the name of the compound and synonym(s), chemical formula, literature reference and transformation matrix. When available, the crystal structure type, crystal habit, cleavages, twinning, color, optical properties, indices of refraction, optical orientation, melting point and transition point are also listed.

THIS EDITION culminates years of effort by J. D. H. Donnay, Johns Hopkins University, Helen M. Ondik, National Bureau of Standards, Sten Samson, California Institute of Technology, Quintin Johnson, Lawrence Radiation Laboratory, Melvin H. Mueller, Argonne National Laboratory, Gerard M. Wolten, Aerospace Corporation, Mary E. Mrose, U.S. Geological Survey, Olga Kennard and David G. Watson, Cambridge University, England and Murray Vernon King, Massachusetts General Hospital.

Shipments are made via insured parcel post. Additional charges for shipments by air or commercial carrier.

TERMS: Domestic—30 days Foreign—prepayment required. Address all orders to:

JOINT COMMITTEE ON POWDER DIFFRACTION STANDARDS 1601 Park Lane, Swarthmore, Pennsylvania 19081

Please accept my order for CRYSTAL DATA, DETERMINATIVE TABLES, Third Edition, Donnay/Ondik.

☐ Organic Volume

☐ Inorganic Volume

Ship to: _____

Signature _____



JCPDS

PERIODICALS

JOURNAL OF RESEARCH reports National Bureau of Standards research and development in physics, mathematics, and chemistry. It is published in two sections, available separately:

• **Physics and Chemistry (Section A)**

Papers of interest primarily to scientists working in these fields. This section covers a broad range of physical and chemical research, with major emphasis on standards of physical measurement, fundamental constants, and properties of matter. Issued six times a year. Annual subscription: Domestic, \$17.00; Foreign, \$21.25.

• **Mathematical Sciences (Section B)**

Studies and compilations designed mainly for the mathematician and theoretical physicist. Topics in mathematical statistics, theory of experiment design, numerical analysis, theoretical physics and chemistry, logical design and programming of computers and computer systems. Short numerical tables. Issued quarterly. Annual subscription: Domestic, \$9.00; Foreign, \$11.25.

DIMENSIONS/NBS (formerly Technical News Bulletin)—This monthly magazine is published to inform scientists, engineers, businessmen, industry, teachers, students, and consumers of the latest advances in science and technology, with primary emphasis on the work at NBS. The magazine highlights and reviews such issues as energy research, fire protection, building technology, metric conversion, pollution abatement, health and safety, and consumer product performance. In addition, it reports the results of Bureau programs in measurement standards and techniques, properties of matter and materials, engineering standards and services, instrumentation, and automatic data processing.

Annual subscription: Domestic, \$9.45; Foreign, \$11.85.

NONPERIODICALS

Monographs—Major contributions to the technical literature on various subjects related to the Bureau's scientific and technical activities.

Handbooks—Recommended codes of engineering and industrial practice (including safety codes) developed in cooperation with interested industries, professional organizations, and regulatory bodies.

Special Publications—Include proceedings of conferences sponsored by NBS, NBS annual reports, and other special publications appropriate to this grouping such as wall charts, pocket cards, and bibliographies.

Applied Mathematics Series—Mathematical tables, manuals, and studies of special interest to physicists, engineers, chemists, biologists, mathematicians, computer programmers, and others engaged in scientific and technical work.

National Standard Reference Data Series—Provides quantitative data on the physical and chemical properties of materials, compiled from the world's literature and critically evaluated. Developed under a world-wide program coordinated by NBS. Program under authority of National Standard Data Act (Public Law 90-396).

BIBLIOGRAPHIC SUBSCRIPTION SERVICES

The following current-awareness and literature-survey bibliographies are issued periodically by the Bureau: **Cryogenic Data Center Current Awareness Service.** A literature survey issued biweekly. Annual subscription: Domestic, \$20.00; Foreign, \$25.00.

Liquified Natural Gas. A literature survey issued quarterly. Annual subscription: \$20.00.

NOTE: At present the principal publication outlet for these data is the Journal of Physical and Chemical Reference Data (JPCRD) published quarterly for NBS by the American Chemical Society (ACS) and the American Institute of Physics (AIP). Subscriptions, reprints, and supplements available from ACS, 1155 Sixteenth St. N.W., Wash. D. C. 20056.

Building Science Series—Disseminates technical information developed at the Bureau on building materials, components, systems, and whole structures. The series presents research results, test methods, and performance criteria related to the structural and environmental functions and the durability and safety characteristics of building elements and systems.

Technical Notes—Studies or reports which are complete in themselves but restrictive in their treatment of a subject. Analogous to monographs but not so comprehensive in scope or definitive in treatment of the subject area. Often serve as a vehicle for final reports of work performed at NBS under the sponsorship of other government agencies.

Voluntary Product Standards—Developed under procedures published by the Department of Commerce in Part 10, Title 15, of the Code of Federal Regulations. The purpose of the standards is to establish nationally recognized requirements for products, and to provide all concerned interests with a basis for common understanding of the characteristics of the products. NBS administers this program as a supplement to the activities of the private sector standardizing organizations.

Consumer Information Series—Practical information, based on NBS research and experience, covering areas of interest to the consumer. Easily understandable language and illustrations provide useful background knowledge for shopping in today's technological marketplace.

Order above NBS publications from: Superintendent of Documents, Government Printing Office, Washington, D.C. 20402.

Order following NBS publications—NBSIR's and FIPS from the National Technical Information Services, Springfield, Va. 22161.

Federal Information Processing Standards Publications (FIPS PUBS)—Publications in this series collectively constitute the Federal Information Processing Standards Register. Register serves as the official source of information in the Federal Government regarding standards issued by NBS pursuant to the Federal Property and Administrative Services Act of 1949 as amended, Public Law 89-306 (79 Stat. 1127), and as implemented by Executive Order 11717 (38 FR 12315, dated May 11, 1973) and Part 6 of Title 15 CFR (Code of Federal Regulations).

NBS Interagency Reports (NBSIR)—A special series of interim or final reports on work performed by NBS for outside sponsors (both government and non-government). In general, initial distribution is handled by the sponsor; public distribution is by the National Technical Information Services (Springfield, Va. 22161) in paper copy or microfiche form.

Superconducting Devices and Materials. A literature survey issued quarterly. Annual subscription: \$20.00. Send subscription orders and remittances for the preceding bibliographic services to National Bureau of Standards, Cryogenic Data Center (275.02) Boulder, Colorado 80302.

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

OFFICIAL BUSINESS

Penalty for Private Use, \$300

POSTAGE AND FEES PAID
U.S. DEPARTMENT OF COMMERCE
COM-215



SPECIAL FOURTH-CLASS RATE
BOOK



75 YEARS
NBS
1901-1976



NIST

3/28/13

237



nbstechnicainote929

A survey
sampling, sa
term stora

