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COMPREHENSIVE ANALYTICAL CHEMISTRY

EDITED BY

D. BARCELÓ

VOLUME XLI

SAMPLE PREPARATION FOR TRACE ELEMENT ANALYSIS

BY

Z. MESTER

R. STURGEON

AMSTERDAM BOSTON HEIDELBERG LONDON NEW YORK OXFORD

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Edited by

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Vol. XXXVIII	Countercurrent Chromatography: The Support-Free Iiquid Stationary Phase
Vol. XXXIX	Integrated Analytical Systems
Vol. XL	Analysis and Fate of Surfactants in the Aquatic Environment

Contents

Series Editor's Preface

This book on Sample Preparation for Trace Element Analysis, edited by Zoltan Mester and Ralph Sturgeon, is a useful addition to the *Comprehensive Analytical Chemistry* series. The impressive number of pages indicates the importance of sample preparation in the area of trace element determination. In a way, it follows the philosophy of a previous book in the series edited by Janusz Pawliszyn (*Sampling and Sample Preparation for Field and Laboratory*, vol XXXVII), and devoted to organic analysis. In that work, the two editors of this volume contributed a chapter on sample preparation for trace element speciation.

It is a pleasure for me to introduce such a comprehensive book with a total of 39 chapters divided in four sections, including several introductory chapters on sampling, calibration, traceability and detection methods. These are followed by 17 chapters dealing with approaches to sample digestion and extraction. This is obviously one of the key issues in sample preparation, and for this reason a variety of chapters that include most of the methods in use – microwaves, solid phase microextraction, membrane extraction, laser ablation, flow injection etc. – are presented. The final 10 chapters cover specific applications to trace element speciation, dealing with different species and matrices, e.g. organotin, mercury, arsenic, metal-based drugs, chromium and also sequential extraction.

The book includes a long list of recognised experts. In addition, many of them are previous contributors to books in this series dealing with speciation. In this respect, the present book is complementary to two previous volumes in the series – vol XXXIII on *Elemental Speciation* edited by Joe Caruso et al. and vol XXXIV on *Discrete Sample Introduction Techniques for Inductively Coupled Plasma Mass Spectrometry* by Diane Beauchemin and co-authors. With the publication of these three books the *Comprehensive Analytical Chemistry* series has extensively covered the area of elemental analysis, speciation and the very important bottleneck of sample preparation. I am sure that all three volumes will be a valuable reference for all researchers working in these fields.

Finally I would like to thank not only the editors of the book but also the various authors for their contributions towards such a comprehensive, unique book on sample preparation for trace element analysis.

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Preface

Two years ago we were asked to write a short review on sample preparation for trace metal speciation as a contribution to a book dealing with general sample preparation issues. Over the course of this work, we realized that this short review was rather an extended table of contents for a future project. We were also acutely aware that there was no comprehensive book devoted to sample preparation on the market dealing with the analysis of samples for trace elements. The stage was thus set.

Following the collection of a sample, every analytical chemist will agree that its subsequent preservation and processing are of paramount importance. The availability of high performance analytical instrumentation has not diminished this need for careful selection of appropriate pretreatment methodologies, intelligently designed to synergistically elicit optimum function from these powerful measurement tools. These were the objectives of this book, to present, in a concise and comprehensive volume, an account of the state-of-the art of this subject matter. When considering the need for publication of a body of work such as this, it is wise to invest time appraising current literature; with the high cost of books, there can be no defense for simply making yet another one available. From our perspective, *Sample Preparation for Trace Element Analysis* was conceived because we believe there was no modern, comprehensive treatise at hand to satisfy the varied needs of the practicing analytical chemist. Without doubt, many of the subject areas targeted in this book have already received in-depth treatment by appropriate monographs. Assembling this knowledge into a single source proves advantageous to the user only if it is accomplished concisely and comprehensively. We hope the reader will vindicate our conclusions.

This book is a multiauthor work, reflecting the diverse expertise arising from its highly qualified contributors. Efforts have been made to maintain a uniformity of style and diction, but readers will agree that the advantages which accrue from the talents of these individuals outweigh that arising from the simple uniformity gained with a single-author treatise. The cooperation of all the contributors in providing material for this book is thus deeply appreciated.

The 39 chapters are authored by international leaders of their fields. The first five chapters deal with general issues related to the determination of trace metals in varied matrices, such as sampling, contamination control, reference materials, calibration and detection techniques. The second part of

the book deals with extraction and sampling technologies (totaling 15 chapters), providing theoretical and practical hints for the users on how to perform specific extractions. Subsequent chapters overview seven major representative matrices and the sample preparation involved in their characterization. This portion of the book is heavily based on the preceding chapters dealing with extraction technologies. The last ten chapters are dedicated to sample preparation for trace element speciation.

Dating from the original discussions with the Publisher, this book has been realised in record time, requiring less than two years to advance from concept to fruition, thanks to excellent work of the over 70 contributing authors and the efforts of the Publisher. The editors and authors hope that readers will find this book useful and instructive and that it will be consulted frequently as a source of information which will make sample preparation less challenging for both the novice and seasoned expert alike.

We wish to acknowledge the support of our home organization: the Institute for National Measurement Standards of the National Research Council of Canada, a stimulating environment and center of excellence for analytical chemistry research.

Finally, we wish to thank the contributing authors for the privilege to work with them on this project and our families their patience and love for having forgone our company on many occasions.

Zoltán Mester
Ralph E. Sturgeon

Acronyms

2-MBT	2-mercaptobenzothiazole
8-HQ	8-hydroxyquinoline
AAS	atomic absorption spectrometry
ACN	acetonitrile
ACP	alternating current plasma
AED	atomic emission detection
AFM	atomic force microscopy
AFS	atomic fluorescence spectrometry
ANOVA	analysis of variance
ARC	anti-reflective coating
AsB	arsenobetaine
AsC	arsenocholine
ASE	accelerated solvent extraction
ASTM	American Society for Testing and Materials
ASV	anodic stripping voltammetry
BEC	background equivalent concentration
CCD	charge coupled device
CCFA	completely continuous flow analysis
CCP	capacitively coupled plasma
CE	capillary electrophoresis
CEA	combustion elemental analysis
CGC	capillary gas chromatography
CL	chemiluminescence
CPG	controlled pore glass
CPX	complexation
CRM	certified reference material
CSV	cathodic stripping voltammetry
CTF	centrifugation
CV	coefficient of variation
CV-AAS	cold vapour atomic absorption spectrometry
CZE-UV	capillary zone electrophoresis ultraviolet spectrophotometry
DAD	diode array detector
DAL	dialkyllead
DBT	dibutyltin
DC arc emission	direct current arc emission spectrometry

DCP	direct current plasma
DCP-OES	direct coupled plasma optical emission spectrometry
DE	diatomaceous earth
DEL	diethyllead
DESe	diethyl selenide
DIN	direct injection nebulizer
DIW	deionized water
DLF-AAS	diode laser flame atomic absorption spectrometry.
DMA	dimethylarsinic acid
DMA(III)	dimethylarsinous acid
DMDSe	dimethyl diselenide
DML	dimethyllead
DMSe	dimethyl selenide
DOM	dissolved organic material
DP-ASV	differential pulse anodic stripping voltammetry
DPCSV	differential pulse cathodic stripping voltammetry
DPhT	diphenyltin
DRC-ICP-MS	dynamic reaction cell ICP-MS
DSI	direct sample insertion
DTA	diethylenetriamine
DZ	dithizone
ECD	electron capture detection
ED-XRF	energy dispersive X ray fluorescence
EI-MS	electron impact ionization mass spectrometry
EL	ethyl lactate
ESI	electrospray ionization
Et	ethyl
ET-AAS:	electrothermal (graphite furnace) atomic absorption spectrometry
EtOH	ethanol
ETV	electrothermal vaporization
EXT	liquid extraction
F-AAS	flame atomic absorption spectrometry
FAB	fast atom bombardment
F-AES	flame atomic emission spectrometry
FIA	flow injection analysis
FID	flame ionization detection
FLD	fluorimetric detection
FPD	flame photometric detection
FT-ICR-MS	fourier transform ion cyclotron resonance mass spectrometry
FTT	filtration
GC(EC):	gas chromatography with electron capture detection
GCB	graphitized carbon black

GC-MS	gas chromatography-mass spectrometry
GD-MS	glow discharge mass spectrometry
GF-AAS	graphite furnace atomic absorption spectrometry
GLP	good laboratory practice
GTF	glucose tolerance factor
HEPA	high efficiency particulate air
HG	hydride generation
HMDE	hanging mercury drop electrode
HMW	high molecular weight
HPA	high pressure ashing
HPLC	high performance liquid chromatography
HRGC	high resolution gas chromatography
HR-ICP-MS	high resolution (sector field) ICP-MS
HSAB	hard-soft acid-base
HT18C6TO	hexathia-18-crown-6-tetraone
HTA	high temperature ash
IAEA	International Atomic Energy Agency
IBMK	isobutyl methyl ketone
IC	ion chromatography
ICP	inductively coupled plasma
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma (atomic) optical emission spectrometry
ICP-QMS	ICP-quadrupole MS
ICP-RC-MS	ICP-reaction cell-MS
ICP-TOF-MS	ICP-time of flight-MS
ID-MS	isotope dilution mass spectrometry
ID-ICP-MS	isotope dilution inductively coupled plasma mass spectrometry
ID-TIMS	isotope dilution thermal ionization mass spectrometry
INAA	instrumental neutron activation analysis (NAA)
IP	ion pair
IR	infra-red
IRMM	Institute for Reference Materials and Measurements
ISE	ion selective electrode
ISO	International Organization for Standardization
ITRS	International Technology Roadmap for Semiconductors
IUPAC	International Union of Pure and Applied Chemistry
KR	knotted reactor
LAS	light absorption spectrometry (molecular UV-visible absorption)
LC	liquid chromatography
LEAF(S)	laser excited atomic fluorescence (spectrometry)

LIBS	laser induced breakdown spectrometry
LiM	lithium metaborate, $LiBO_2$
LIMS	laboratory information management system
LiT	lithium tetraborate, $Li_2B_4O_7$
LLE	liquid-liquid extraction
LMW	low molecular weight
LOD	limit of detection
LOV	lab-on-valve
LRM	laboratory reference material
LSASV	linear sweep anodic stripping voltammetry
LSE	liquid-solid extraction
LTA	low temperature ashing
MA	methylarsonic acid
MA(III)	methylarsonous acid
MALDI	matrix assisted laser desorption mass spectrometry
MBE	molecular beam epitaxy
MBT	monobutyltin
Me	methyl
MEKC	micellar electrokinetic chromatography
MeOH	methanol
MIP	microwave induced plasma
MLS	master laboratory station
MMA	monomethyarsonic acid
MMLLE	microporous membrane liquid-liquid extraction
MOCVD	molecular organic compound vapor deposition
MPD	microwave-induced plasma detector
MPhT	monophenyltin
MPT	microwave plasma torch
MS	mass spectrometry
MT	metallothionein
MW	microwave
NAA	neutron activation analysis
NCH	neocuproine
NIES	National Institute for Environmental Studies
NIOSH	National Institute of Occupational Safety and Health
NIST	National Institute of Standards and Technology
Nl	measured gas volume in liter at 0°C.
NMR	nuclear magnetic resonance
NRCC	National Research Council of Canada
NSOM	near-field scanning optical microscopy
NWA	non-wetting agents
ODETA	4-(N-octyl)diethylenetriamine
OES	optical emission spectrometry
OLR	ordinary linear regression

OXI	oxidation
PA	polyacrylate
PAA	photon activation analysis
PAAM	piconilic acid amide
PADMAP	2-(2-pyridylazo)-5-dimethylaminophenol
PAH	polyaromatic hydrocarbon
PAR	4-(2-pyridylazo)-porphyrin
PBMS	performance based measurement system
PDMS	polydimethyl siloxane
PE	polyethylene
PEC	power and event controller
PGC	porous graphitized carbon
Ph	phenyl
PIXE	proton induced x-ray emission spectrometry
PP	polypropylene
PR	photoresist
PS-MS	plasma source mass spectrometry
PTFE	polytetrafluoroethylene
PTV	programmed temperature vaporization
PUF	polyurethane foam
PVC	polyvinylchloride
P-XRF	portable XRF
QA	quality assurance
QCM	quality control material
QF-AAS	quartz furnace atomic absorption spectrometry
QMS	quadrupole mass filters
QTA	(heated) quartz tube atomizer
QZ	quartz
RCC	residual carbon content
REE	rare earth element
RM	reference material
RNAA	radiochemical separation neutron activation analysis
ROMP	ring-opening metathesis polymerization
RP	reverse phase
RSD	relative standard deviation
RTD	resistance temperature detector
SA	salicylic acid
SDS	sodium dodecyl sulfonate
SEC	size exclusion chromatography
SE-FLR	solvent extraction fluorometry (molecular)
SEP	sequential extraction procedure
SF	supercritical fluid
SFE	supercritical fluid extraction
SF-ICP-MS	sector field ICP-MS

SGBM	silica gel bound macrocycles
SI	Systéme International
SI	sequential injection
SIA	sequential injection analysis
SIM	selected ion monitoring
SIMS	secondary ion mass spectrometry
SLM	supported liquid membrane extraction
SPE	solid phase extraction
SPME	solid phase microextraction
SPS	solid phase spectrophotometry
SRM	standard reference material
SS-MS	spark source mass spectrometry
STAT	slotted tube atom trap
T_4BPP	tetra-(4-bromophenyl)-porphyrin
TAL	trialkyllead
TBT	tributyltin
TCD	thermal conductivity
TCLP	toxicity characteristic leaching procedure
TD	thermodesorption
TeAL	tetraalkyllead
TeEL	tetraethyllead
TEL	triethyllead
TeML	tetramethyllead
TFA	trifluoroacetylacetone
THET-AAS:	transverse heated graphite atomizer ET-AAS (THGA: transverse heated graphite atomizer)
THF	tetrahydrofuran
TIMS	thermal ionization mass spectrometry
TMAB	tetramethylammonium bromide
TMAO	trimethylarsine oxide
TML	trimethyllead
TMOS	tetramethoxy silane
TOF-MS	time of flight mass spectrometry
TPB	tetraphenylborate
TPhT	triphenyltin
TprT	tripropyltin
TS-FF-AAS	thermospray flame-furnace AAS
T-XRF	total reflection XRF
UE	ultrasonic extraction
ULPA	ultra low penetration air
UPW	ultrapure water
US	ultrasound
US EPA	United States Environmental Protection Agency
UV-VIS	ultraviolet visible spectrometry

VG	vapor generation
VMC	volatile metal(loid) compound
VOCs	volatile organic compounds
VOL	volumetry (titrimetry)
VPD	vapor phase deposition
WHO	World Health Organization
WLR	weighted linear regression
XRA	X-ray absorption
XRF	X-ray fluorescence spectrometry
ZHE	zero headspace extraction

Chapter 1

Sampling and sample preservation for trace element analysis

Byron Kratochvil

1.1 INTRODUCTION

Modern analytical methods and instrumentation make possible the measurement of increasingly smaller concentrations of even the most complex molecules and species in complex matrices. This has increased the importance of collecting, storing, and processing samples for analysis in a manner that keeps them as unaltered and contamination free as possible. In addition, improved measurement techniques and tools allow, or often require, the use of smaller analytical test portions to determine analyte concentrations. Small test portions mean more difficulty in achieving representativeness of the population, especially when analyzing for trace components.

First of all, the quality of any analytical result depends on sample representativeness and integrity. Although many sources of error in an analysis can be controlled through use of blanks, standards, or reference samples, neither blank nor standard can repair the damage caused by an invalid sample. Keith [1], in the preface of a book on environmental sampling, says:

> "The logic is simple. If the right kinds of samples are not collected from the right areas at a site and then preserved, prepared, and analyzed correctly, wrong answers will be obtained. They may be precise and accurate answers, but they will be wrong in that they will not represent the condition of the site with respect to the absence, presence, or representative concentrations of the pollutants of interest."

Keith's statement applies with equal validity to all analytical sampling operations regardless of analyte, concentration, or matrix.

This chapter outlines some general principles of sampling design and sample preservation. Specific sampling and sample preparation procedures for various matrices and individual elements are treated in subsequent chapters. A brief bibliography and glossary of selected sampling terms are provided at the end of this chapter.

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1.2 PRELIMINARY CONSIDERATIONS

1.2.1 Sampling variability

When obtaining an estimate of the uncertainty in an analytical result, the uncertainty in the sampling step is often significant, and frequently far larger than the measurement uncertainty. For random errors, the overall standard deviation, s_o, is related to the standard deviation for the sampling operation, s_s, and to that for the remaining analytical operations, s_a, by:

$$s_o^2 = s_a^2 + s_s^2 \tag{1.1}$$

Measurements should be designed insofar as possible to allow the separate evaluation of sample and measurement variability. For measurements in a state of statistical control, s_a can be determined by the analysis of reference materials or standards. Then, s_s can be obtained from Eq. (1.1), because s_o is obtained by analysis of a series of samples. Alternatively, a set of replicate measurements on samples may be designed to evaluate both s_a and s_s.

Youden [2] noted that further reduction in the analytical uncertainty is unimportant once it is one-third or less of the sampling uncertainty. So, if the sampling uncertainty is large, use of a rapid, approximate analytical method may be faster, simpler, and permit more samples to be tested, thereby reducing overall uncertainty without increasing time or effort.

1.2.2 Sampling strategies

Sampling strategies may be classified as judgmental (intuitive), statistical, or systematic. Judgment sampling relies on general knowledge gained by experience with the population (or similar ones). Therefore, any conclusions drawn from the resulting data are necessarily intuitive, in part. Statistical sampling is based on all parts of the population having an equal chance of being selected. With a statistical sampling strategy, conclusions may be drawn based on statistical probabilities. In systematic sampling, the sample increments are collected in a regular pattern throughout the population. It has the advantage that execution is usually more straightforward and less expensive.

Protocol sampling is a form of sampling specified in defined circumstances, often by regulatory agencies or by groups, such as the American Society for Testing and Materials (ASTM), as a basis for decision-making in legal and commercial matters. For example, regulations may specify detailed sampling procedures, which, if not followed, could make the sample invalid for the intended purpose. The sampling procedure may be intuitive, statistical, or a combination, but must be followed explicitly.

1.2.3 Uncertainties in sampling

Sampling uncertainties may arise either from the properties of the population, and therefore inherent to any sample taken from it, or from the sampling operation itself. These uncertainties may be reduced, but never completely eliminated, by careful execution of a properly designed sampling plan that incorporates identification of the population and sampling sites, along with the procedures required to deliver an uncontaminated, representative sample to the analytical laboratory.

An important source of sampling uncertainty is systematic, non-random, bias caused by exclusion or inclusion in the sample of some components of the population over others owing to differences in size, mass, location, stickiness, and so on. Another is sample contamination or change during collection, transport, storage, or preparation for analysis (this topic is discussed in Section 1.6). Poor design or improper use of sampling equipment may also introduce bias, as may the omission of collateral measurements, such as flow rate or pressures, that affect results.

1.3 TYPES OF SAMPLES

1.3.1 Judgment samples

Judgment samples are samples collected from a population on the basis of experience, intuition, and knowledge of the history or properties of the population (or related ones). Sometimes, the goal is to obtain a single sample that may be termed "representative" to connote that it is expected to exhibit the average properties of the population.

Collection of a single sample may have validity in situations where the population is essentially homogeneous or made so prior to sample collection. It may also be legitimate when random sampling is difficult or impossible owing to safety or cost considerations. Under these conditions, however, the shortcomings of the sampling operation and the limitations in data treatment should be clearly stated. Generally, a plan based on at least some elements of random sampling is recommended.

Judgment sampling requires assumptions about the degree to which the samples may be considered representative. Because the validity of the assumptions depends on the experience of the one making them, it is difficult to know the degree to which they are acceptable for a given application. A major advantage of judgment sampling is that it is usually less costly than rigorous random sampling. For regulatory or legal purposes, however, personal bias should be reduced or eliminated as much as possible. Often a combination of judgment and random sampling provides the best compromise between unacceptable costs and data quality.

1.3.2 Random samples

Analyses are almost always performed to obtain information about a population that is larger than the test portions being measured. If the samples under examination are biased, inferences made from them will be biased. The difference between the target population to which conclusions are applied, and the samples from which the test portions for analyses are drawn, may be minimized by selecting samples in a manner that gives each part of the population an equal chance of selection. This process, called random sampling, allows the user of the resulting analytical data to make statistical generalizations based on mathematical probabilities.

Selecting truly random samples is difficult; random in this context does not mean haphazard. A recommended method for a population consisting of units such as pharmaceutical tablets is to use random numbers to select units for analysis. Each unit is assigned a number, and units are selected by use of a random number generator.[1] Bulk materials may be divided into a number of real or imaginary segments; the segments may be areas on a two-dimensional surface or volumes for a three-dimensional population.

Data obtained by measurements on random samples can be analyzed by statistical methods to identify whether systematic relations among results exist due to trends or biases in the measurements.

1.3.3 Systematic samples

Because of its simplicity, sampling at evenly spaced intervals over a population is often used in place of random sampling. The criterion that all parts of the population have an equal chance of selection may be satisfied for evenly spaced sampling by imposing a random start time or sampling location on the process. This allows the application of classical statistical tests to the data. A potential problem with systematic sampling is that results may be biased if the analyte of interest is distributed in a periodic fashion within the population.

It is also sometimes useful to collect samples in a systematic manner to reflect or test a hypothesis, such as the presence of systematic changes in population composition with time, temperature, or spatial location. Under specified conditions, each sample may be considered as a separate discrete population but the results may still be statistically tested for the significance of apparent differences.

[1] Random numbers may be obtained from several sources on the Internet. A good example is http://www.fourmilab.ch/hotbits/, which generates sequences of random numbers based on radioactive decay of krypton-85. A Geiger–Muller tube is interfaced to a computer and the times between successive pairs of radioactive decays measured and provided as bytes. Once the bytes are delivered, they are discarded.

1.3.4 Subsamples

Field samples are typically placed in containers and sent to the laboratory for further processing. Sometimes, transport of all the field increments to the laboratory is deemed too inefficient or costly. In this case, the increments may be homogenized, after crushing or grinding if needed, and subsampled on site prior to transport. The work needed to reduce particle size, blend, or otherwise to process a bulk field sample before withdrawing subsamples for analysis depends on the variability in composition of the material constituting the original sample and on the extent of mixing required. Care must be taken to avoid contamination or loss that may introduce bias. Generally, processing and subsampling in a clean, controlled environment whenever possible provide better quality control.

When subsampling is done in the field, the sampling plan, discussed in Section 1.4.2, should specify that the sampler have sufficient training and knowledge of sampling theory to subsample properly. Also, the analyst should be provided with all available information on prior subsampling and homogenizing operations.

1.3.5 Composite samples

Sometimes, increments are combined to produce a laboratory sample that is defined as representative. Advantages of compositing include reduced sample handling and analytical effort. It provides an estimate of the average concentration of the analyte, but not of its distribution. A variety of sampling systems and mixing procedures have been developed to produce composites from both liquid and solid materials.

Compositing of increments is attractive when costs of analytical measurements are greater than the costs of sampling. But potentially useful information, such as the presence of hot spots, may be lost. Analysis of individual increments allows not only estimation of the distribution of the analyte within the population, but also evaluation of apparent differences within and among samples. Garner et al. [3] discuss the advantages and limitations of composite sampling for environmental monitoring.

1.4 PLANNING THE SAMPLING OPERATION

1.4.1 Defining goals

Several key decisions should be made before sampling is initiated. These include defining the population to be studied, the substance(s) to be measured, the precision required in the result, and the extent to which speciation and distribution within the population is needed. Any assumptions about the population should be clearly identified. Decision-makers should preferably

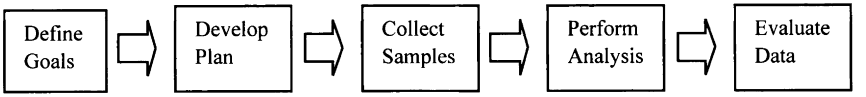

Fig. 1.1. Elements of the overall analytical process.

include the client for the data, sampling personnel, the person responsible for the analytical work, and someone knowledgeable about statistics.

Decisions made at this point establish the goals of the work, and are the first step in the overall analytical process (Fig. 1.1). With this information in hand, a viable sampling plan can be drafted.

1.4.2 Sampling plans

The wide variety of populations sampled for chemical analysis makes the establishment of a single overall protocol impossible; accordingly, each matrix requires its own sampling plan. Often, regulatory agencies issue documents covering analytical methodologies that include sampling procedures. Examples include the US Environmental Protection Agency (US EPA), the International Organization for Standardization (ISO), and the ASTM. In addition, many specialty groups, such as the American Water Works Association, provide information on sampling protocols, tools, and techniques applicable to specific matrices. Where the analytical data may involve potential legal issues regarding compliance with environmental regulation, with workplace safety, or with commercial contract agreements, protocols recommended by recognized associations or agencies should be used whenever possible.

All valid sampling plans and protocols have basic elements in common. These elements include specification of the size, number, and location of sample increments, the extent of compositing where warranted, and steps for subsampling (after particle size reduction, if applicable, and mixing) of the initial increments to produce laboratory samples and test portions. The plan should be in the form of a written protocol that includes procedures for all steps, from initial sample collection to final preparation of test portions for analysis. The protocol should tell when, where, and how to collect sample increments. It should include criteria for rejection of material not part of the population, as for example stones above a defined size in a soil sample being analyzed for available trace nutrients. It should also specify who performs the sampling, sample logging and chain of custody procedures, the type and size of containers to be used, cleaning procedures for equipment and containers, preservatives, conditions of sample storage and, as appropriate, auxiliary information such as temperature or flow velocity in a stream. It should also list the qualifications and training required of the personnel carrying out the operations. A checklist, adapted from Ref. [4], is provided in Table 1.1.

TABLE 1.1

Checklist for elements of a sampling protocol (after Ref. [4])

Apparatus and equipment checklist
- Sampling tools and apparatus
- Sample containers of appropriate type, material, and size
- Cleaning supplies for tools, equipment, and containers
- Preservatives, including provision for cooling of samples if necessary
- Labels, tape, waterproof pens, packaging materials
- Chain of custody forms, sample seals, log books
- Safety equipment, including protective clothing

Instructions checklist for presampling
- Recording of observations at sampling sites
- Cleaning of apparatus before and after sampling
- Calibration of apparatus
- Cleaning and handling of sample containers
- Safety procedures
- Procedure if problems prevent strict adherence to protocol

Instructions checklist for sampling
- Number, type, and size of exploratory, regular, and quality assurance samples
- Number, type, and size of sample increments
- Procedure for identifying locations from which increments are to be collected
- Procedure for operation of apparatus and collection of increments
- Special sampling precautions or conditions of collection, including criteria for rejection of foreign material
- Procedure for compositing, if applicable
- Use of preservatives

Instructions checklist for postsampling
- Completion of auxiliary information on sample labels and in logbooks
- Chain of custody forms
- Sample packaging, transport, and conditions for travel and storage, including maximum holding time for samples prior to analysis

General
- Information on analytical methods, limits of detection, interferences

Once the sampling plan is drafted, it is worthwhile to have it reviewed by independent experts. This is especially important when assumptions have been made, or when all or part of the plan is based on judgment. For populations whose characteristics are little known, time and effort may be saved by collecting and analyzing a preliminary set of samples, using experience and intuition as a guide to make them as representative as possible. On the basis of this information, a more efficient and cost-effective plan can be prepared.

Where feasible, it is useful to have the analyst perform or supervise the sampling operation. Otherwise he or she should, in addition to helping prepare the written protocol, ensure that the sample collectors are well trained and understand the importance of each step so that bias and contamination are minimized. The training should emphasize the importance of accurate sample labeling and logging, and of a chain of custody to ensure sample integrity from collection to measurement.

For bulk materials, local homogeneity affects sample size. Increments should be large enough to not be biased with respect to the different sizes and types of particles present in the material. Where available sampling equipment precludes collection of larger increments, two or more smaller ones may be taken adjacent to each other. These may be composited or analyzed separately. (Separate analysis can provide information on the extent of local heterogeneity.)

When sampling a material whose properties are unknown, a good approach is to collect a small number of exploratory samples, using experience and judgment to make them as representative as possible, and analyze them for the substance of interest. From this preliminary information, a more refined sampling plan can be developed.

1.5 STATISTICAL SAMPLING

1.5.1 Introduction

Statistics provides a number of useful tools to assist in determining how many sample increments to take from a population, how large they should be, and from where they should be taken in order to hold the sampling uncertainty to some specified level with a given level of confidence. Most statistical sampling theory is based on the population having a normal (Gaussian) distribution, but other distributions, such as lognormal, do occur in nature.

1.5.2 Minimum number of increments

Unless a population is known to be homogeneous, a valid sampling plan requires collection of increments from multiple locations. Assuming, for the moment, negligible measurement uncertainty relative to that for sampling, Provost [5] describes the minimum number of increments, n_s, needed to hold the sampling uncertainty, E_s, to a given level of confidence by the relation:

$$n_s = (z\sigma_s/E_s)^2 \tag{1.2}$$

where z is a stated level of confidence, say 95%. In most applications, σ_s is either known from past history of the population or can be estimated from measurements on a set of preliminary samples to obtain values of s_s and X.

(Remember that if measurement uncertainties are not negligible relative to those of the sampling operations, then s_s should be calculated by Eq. (1.1).)

Since

$$\mu = -X \pm (ts/\sqrt{n}) \tag{1.3}$$

where t is obtained from statistical tables as an estimate of z from n measurements, the maximum acceptable sampling uncertainty, E_s, can be defined by:

$$E_s = |\mu - X| = ts/\sqrt{n_s} \tag{1.4}$$

Rearranging,

$$n_s = (ts_s/E_s)^2 \tag{1.5}$$

Initially, t can be set at 1.96 for 95% confidence limits and a first estimate of n can be calculated. The t-value for this n is then substituted and the system iterated to constant n.

1.5.3 Minimum size of increments in well-mixed particulate populations

When sampling well-mixed populations of heterogeneous particles, as is often encountered in the subsampling of laboratory samples, Ingamells and Switzer [6] showed the relation:

$$WR^2 = K_s \tag{1.6}$$

to be applicable. Here W is the weight of sample analyzed, R is the relative standard deviation of sample composition in percent, and K_s is a constant equal to the weight of sample required to limit the sampling uncertainty to 1% relative with 68% confidence. In practice, K_s is determined by estimating s_s from a series of samples of weight W. Once K_s is known, the minimum sample weight, W, required for any maximum relative standard deviation can be calculated. For poorly mixed or stratified materials, the calculated value of K_s increases as W increases. This provides a way of testing the homogeneity of the population.

When sampling a mixture of particles, it is important to collect enough of each particle type to ensure representativeness. In some cases, where the element under test is present as only a small fraction of the particles (as in elemental gold or diamond deposits), quite large bulk samples must be taken, and particle size reduction and thorough mixing must be conducted before subsampling. For such populations the sampling standard deviation, $\sigma(g_1)$, may be calculated using the Johnson equation [7]:

$$\sigma(g_1) = \left\{(\pi d_1 g_1/6)\left[\sum f_i(2r_i)^3\right]\right\}^{1/2} \tag{1.7}$$

where g_1 is the mass and d_1 is the density of the sample particles containing the trace component, f_i is the fraction by mass of the trace element in particle size class i, and r_i is the radius of particles containing the trace element.

If the element of interest is present in each of a mixture of two types of particles but the fraction of one type is small, Zheng and Kratochvil [8] have shown that a combination of the Johnson equation with one developed by Bennedetti-Pichler [9] is applicable. Here the standard deviation, σ_P, expressed in percent, is given by:

$$\sigma_P = [(P_1 - P_2)/g]\left\{(\pi d_1/6)\left[\sum f_i(2r_i)^3\right]g_1\right\}^{1/2} \tag{1.8}$$

where P_1 and P_2 are the percentages of the trace element in each of the two types of particles in the mixture, g is the mass of sample, g_1 is the mass of the fraction of type 1 particles, and d_1 is the density of the type 1 sample particles. The remaining terms are as defined in Eq. (1.7).

Equations (1.7) and (1.8) show that the sampling standard deviation varies as the square root of the sample mass and number of particles. This means that for every 10-fold decrease in the percentage of sought for substance, test-portion size must increase 100-fold for a given level of sampling error and particle size. It is therefore especially important that laboratory samples for trace analysis are adequately ground and mixed prior to removal of test portions for trace analysis.

The general approach described in this section has been extended by Gao and Kratochvil [10] to the calculation of sampling uncertainty for well-mixed materials containing more than two types of particles.

1.5.4 Sample increment size in segregated populations

Visman [11] demonstrated that for some segregated materials the variance of sampling could be expressed by:

$$\sigma_s^2 = (A/wn) + (B/n) \tag{1.9}$$

The constant A is related to Ingamells' subsampling constant K and the average composition of the analyte, x_{av}, by $A = 10^4 x_{av}$. The constant B is related to the degree of segregation of the population. Values of A and B must be obtained experimentally from the bulk population. This can be done in two ways. In the first, two sets of sample increments are collected, one with w as small as, and the other as large as, feasible. The two sets are analyzed, the sampling variances calculated and substituted into Eq. (1.9) to give values for A and B. In the second, arising out of published discussions by Duncan and Visman [12], Visman proposed collection of a set of increment pairs, each pair of increments being of the same weight and taken from adjacent sites in the population. From the analytical data on the increments, an intraclass correlation coefficient, r, is calculated, either directly or by ANOVA [13]. Values for A and B are then

calculated from Eq. (1.9) and the relation $r = Bm/A$, where m is the average particle mass. Increasing either W or N will reduce uncertainty due to random variability, but only increasing the number of increments, n, will reduce uncertainty due to segregation.

All the sampling equations discussed in this section have been derived for normally distributed populations. As mentioned earlier, not all populations follow a Gaussian distribution. Procedures to test data for normality and for dealing with non-normality by data transformation or use of other procedures or distribution functions are available in the statistical literature.

Problems may arise when small regions of a population contain analyte in much higher concentrations than elsewhere. This so-called "nugget" or "hot spot" effect is often encountered when sampling populations such as gold ores or contaminated industrial sites, but it can also be a factor in less obvious situations. An example is microanalytical investigation of surfaces using current sophisticated microtechniques. In situ analytical measurements on heterogeneous surfaces with a probe only a few micrometers in diameter may produce significant errors if areas of unusually high or low concentration are missed or oversampled. There is also the danger that an unusually high result from a hot spot may be rejected as an anomalous outlier. The sampling plan should take into account the possibility of encountering hot spots and their potential effect on the goals of the sampling program.

1.5.5 From where should increments be taken?

The variety of populations of analytical, and therefore sampling, interest encompasses every part of nature and human activity. To ensure that all parts of a population have an equal chance of being selected for analysis requires a random element in the sampling strategy (see Section 1.3.2). Several strategies have been proposed to meet this requirement. These include, in addition to simple random sampling, systematic grid sampling with a random initial start point or with random sampling within individual grid areas or volumes. To improve sampling efficiency, other sampling schemes, including stratified, cluster, and two-stage sampling, have been developed.

In simple random sampling, the target population is divided on paper into a set of units and a defined number of the units are randomly selected for sampling. The units may be one dimensional, as a drill core or objects on a production line; two dimensional, as an agricultural field or a surface film coating on a manufactured product; or three dimensional, as a lake, railway tank car, or the atmosphere in an industrial plant.

In systematic grid sampling, the population is divided into a two- or three-dimensional grid and samples are collected from within each grid area or volume. Systematic sampling is often used to increase the probability of locating possible hot spots in a population. It has little inherent bias but may require more samples to be as effective as random sampling.

In two-stage sampling, primary blocks or units are randomly selected within the population and two or more sample increments taken from locations within each unit. The locations may be selected systematically or randomly.

Stratified random sampling involves division of the population into sections called strata. The number, size, and shape of strata are important to the design of an efficient and cost-effective sampling plan. If the goal is to estimate more precisely the average analyte concentration in the population, then each stratum should be as uniform in the elements of interest as possible. This reduces the number of sample increments needed to define analyte distribution within each stratum. If analyte distribution among separate strata is of interest, then the sampling plan may involve judgment as to size and location of the strata.

In cluster sampling, a number of increments are collected from one or more small sections of the population. This method is used when specific sections have been identified, either through judgment or by previous sampling, to be likely to contain more of the substance of interest.

1.5.6 Model-based sampling

The sampling equations discussed in previous sections are all based on classical sampling theory, such as described by Cochran [14] and others. This approach, sometimes called design-based sampling, makes no assumptions about the population other than that it is fixed. Many sampling methodologies and statistical tools have been developed to handle various population distributions within this classical framework.

A second approach, termed model-based sampling, employs one of several types of models to describe variability within a population. This methodology is most developed in the area of geostatistics. Borgman et al. [15] propose that, since the model-based approach views randomness as a property of a population, pure random sampling is no longer required and, in fact, may not be desirable because regularly spaced observations usually provide the best information about the degree of randomness present. A drawback is that the model must include information on expected patterns of variability within the population, though these patterns need not be completely understood to achieve reliable results.

The biggest applications of model-based sampling have been for geostatistical estimations of underground ore reserves, but the method has also been applied to environmental studies [16]. A widely used form, called kriging, assumes a linear trend in concentration of the sought-for element.

A sampling approach that includes elements of model design has been developed by Gy [17]. Although Gy employs classical random sampling statistics, he systematically considers all possible errors that might be encountered in the collection of a valid sample, including population variability, prior to sampling. In effect, Gy recommends incorporation of all uncertainties

that may affect representativeness of samples into the sampling design rather than assuming that randomness is the only source of variability.

1.5.7 Balancing economic factors and purpose of data collection against sample quality

Sampling is often costly, especially in terms of time commitment by trained personnel. Therefore, the sampling plan should consider ways of minimizing the cost and variance of the sampling operation. Suppose a stratified sampling design is formulated consisting of n_1 strata with n_2 samples taken from each stratum and n_3 analytical measurements on each sample. For strata equal in size and variance, the cost of determining a population mean to within a desired variance may be minimized as follows.

The total cost of the operation, c, is equal to the sum of the cost of selecting the strata c_1, sampling within the strata c_2, and performing the analysis c_3:

$$c = n_1c_1 + n_1n_2c_2 + n_1n_2n_3c_3 \tag{1.10}$$

The overall variance for the population may be expressed as the sum of the variance contributions from the two stages of sampling and analyses:

$$\sigma^2 = \frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_1n_2} + \frac{\sigma_3^2}{n_1n_2n_3} \tag{1.11}$$

Bennett and Franklin [18] show that to minimize the total cost for a preselected overall variance, the values of n_1, n_2, and n_3 may be found from:

$$n_1 = \frac{\sqrt{\sigma_1^2/c_1}}{\sigma^2}\left(\sqrt{\sigma_1^2c_1} + \sqrt{\sigma_2^2c_2} + \sqrt{\sigma_3^2c_3}\right) \tag{1.12}$$

$$n_2 = \sqrt{\frac{\sigma_2^2c_1}{\sigma_1^2c_2}} \tag{1.13}$$

$$n_3 = \sqrt{\frac{\sigma_3^2c_2}{\sigma_2^2c_3}} \tag{1.14}$$

Note that the optimum allocation of sampling effort after the first stage is independent of the desired overall variance. This means that when the goal is reduction in overall variance at minimum cost, one should increase the number of strata sampled and hold the other steps constant.

Similarly, for a fixed total cost; it was shown by Marcuse [19] that the optimum value for n_1 is given by:

$$n_1 = \frac{c\sqrt{\sigma_1^2/c_1}}{\sqrt{\sigma_1^2c_1} + \sqrt{\sigma_2^2c_2} + \sqrt{\sigma_3^2c_3}} \tag{1.15}$$

while the optimum values for n_2 and n_3 continue to be given by Eqs. (1.13) and (1.14). Thus, the optimum allocation beyond the first stage is the same for fixed total cost as for fixed total variance. The same principles can be applied to any number of stages in a nested sampling design.

If strata are not equal in size or in distribution of the analyte, appropriate weighting factors must be incorporated into these expressions.

1.6 SAMPLE HANDLING AND PRESERVATION DURING COLLECTION, TRANSPORT, AND STORAGE

1.6.1 Handling and storage of samples

Samples may undergo a variety of chemical or physical changes during collection, transport, storage, and preparation for analysis. Changes may include loss of sample through volatilization, chemical reactions among components of the sample, or reaction of sample components with sampling tools, sample containers, or transfer lines. Other sources of change include reactions of sample components with external agents such as oxygen, carbon dioxide, or water in the atmosphere, or with sampling equipment or containers. Decomposition during transport or storage may occur as a result of high temperatures or microbial action. Errors from these sources can be minimized by protecting samples from exposure to external agents, and by reducing rates of reaction through addition of preservatives and/or maintaining samples at low temperatures. Preservatives reduce decomposition by altering pH, redox conditions, or solubility; by converting species of interest into more stable forms; by blanketing or coating samples to prevent reaction; or by acting as biocides. Care must be taken that preservatives do not interfere with subsequent analytical measurements. In fact, the best preservation method is storage at temperatures that are as low as possible. Most materials may be stored without change for years at liquid nitrogen temperature (-196°C), though this method is costly and often difficult to implement.

Since samples may begin to change from the time they are taken, analysis should ideally be done immediately after collection. Where the analysis involves digestion or extraction, consideration should be given to implementing this step promptly after collection, then storing the processed sample until measurement can be made.

Procedures for sample collection, preservation, and storage are available from a variety of sources, such as the US Environmental Agency, for sampling of the environment, and the ASTM and ISO for industrial and commercial materials. An example of some of the recommendations provided by the US EPA for the evaluation of inland water and sediments is given in Table 1.2.