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THE UNIVERSITY OF ALBERTA

STATISTICS OF SAMPLING FOR ATHABASCA OIL SAND AND MODEL POPULATIONS

by

E. Dean Wallace

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

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March 7, 1989

Dean Wallace
Alberta Research Council
Clover Bar, Alberta

Dear Dean:

This letter authorizes you to include the following article as an appendix in your doctoral thesis:

> "Sampling for Chemical Analysis", published in Analytical Chemistry, 1984, <u>56</u>, 113R-129R and authored by Byron Kratochvil, Dean Wallace, and John K. Taylor.

Sincerely,

B. Kratochvil

B. Kratochvil
Professor

BK:co

BASF Canada Inc.

BASF

Dispersions

March 8, 1989

Mr. Dean Wallace
Manager, Oil Sand Sample Bank
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Dear Dean:

I give permission to reprint the following material in your Ph. D. thesis.

> Schematic diagram showing a refined model of Athabasca oil sand, which appeared in Figure 10 of "Microscopic Structure of Athabasca Oil Sand" by K. Takamura, Canadian Journal of Chemical Engineering, Vol. 60, p. 543 (1982).

Sincerely yours,

Koichi Takamura
Science Advisor

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MESSAGE

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March 13, 1989

Mr. Dean Wallace
Alberta Research Council
Edmonton, Alberta
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Dear Mr. Wallace:

This will confirm that you have my permission to include any part or all parts of the publication, "Sampling for Chemical Analysis" by Kratochvil, Wallace, and Tay Anal. Chem. 56, 113R (1984), in your thesis.

Yours sincerely,

John K. Taylor

John K. Taylor, Ph.D.
Guest Scientist

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled:

STATISTICS OF SAMPLING FOR ATHABASCA OIL SAND AND MODEL POPULATIONS

submitted by E. Dean Wallace in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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Date: March 3, 1989

TO SHELLEY, ERIN AND LAUREN

WE DID IT!

ABSTRACT

The variability in the level of bitumen, solids and water in multi-tonne lots of Athabasca oil sand is often a greater contributor to uncertainty in analytical data than errors in the measurement stage of the analysis.

A mechanical mill and spinning subsampler that produce 135-g test portions from 1-kg laboratory samples of oil sand is evaluated using a factorial experimental design. Small bias errors resulting from evaporative loss of water and selective retention of bitumen in the mill are identified. Subsampling plus analytical uncertainty is less than 0.2% when the mill/subsampler is used to obtain test samples and the major components are separated by a modified Soxhlet extraction.

Sampling constants originally defined by Visman and representing the random and segregation distribution of components in a population are defined for bitumen, solids and water in Athabasca oil sand. In the sampling of minerals the size of particles defined by physical methods such as sieving controls sampling uncertainty. A "theoretical particle" size of 20 g defined for mined samples of Athabasca oil sand proves that particles do not necessarily correspond to a physical entity in a material.

Sampling experiments and calculations that define whether a population is well-mixed or segregated are identified. The effect of changing increment size on sampling variance is predicted graphically for populations of known average particle size and degree of segregation.

Sampling experiments carried out on one-dimensional arrays generated by a computer prove that the approach to sampling used for Athabasca oil sand is inappropriate when the component of interest in a population exists in a periodic pattern. If the component is present in patches, sampling variance is controlled by the ratio of increment size to patch size and is not accurately represented by the general equation of Visman. Nevertheless, the Visman equation can be applied in many cases because patch sizes and composition are not as clearly defined in nature as they are in simple mathematical arrays.

ACKNOWLEDGMENTS

The commitments from many individuals and organizations were vital to the completion of this research project. I thank the management of the Oil Sands and Hydrocarbon Recovery Department of the Alberta Research Council for their logistical and spiritual support and the Alberta Oil Sands Technology and Research Authority for their financial support through the Oil Sands Sample Bank. In particular, I thank Mr. John Starr and Mr. Gary Martin who made the initial commitments to the study and Mrs. Deborah Henry who has ensured that my responsibilities at the Alberta Research Council were met during my attendance at the University of Alberta over the past six years.

I am especially grateful to Dr. Byron Kratochvil for his support, understanding, direction and the desire for learning that he has instilled in me. I thank his research group and Mr. Robert Shaw in particular for the fruitful scientific discussions and helpful suggestions.

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B	Visman's sampling constant that describes the contribution to sampling variance of the segregated distribution of a component
c	Gy's composition factor
d	patch density (Equations 39 to 41)
$\bar{d}$	average density
d_g	density of the gangue
d_x	density of the component of interest
d_1, d_2	densities of two types of particles
D_i	Kolmogorov's deviation from a Gaussian distribution for the ith data point in a series of data points ranked from i=1 to i=n
f	Gy's shape factor
g	Gy's particle size distribution factor
i	number of increments
i_{Sm}, i_{Lg}	number of small and large increments (Equations 27 to 29)
j	number of replicate analyses per increment
k	number of replicates per trial in a factorial experiment
K_s	Ingamells' sampling constant
l	Gy's liberation factor
m	number of trials in a factorial experiment (Table 2)
m	reciprocal of average particle mass
$[min]$	minimum significant effect in a factorial experiment
n	number of particles (Equation 3)
n	number of increments (Equations 6, 11 and 17)

p	fraction of a selected type of particle in a mixture
p	number of pairs of increments (Equation 13)
p	frequency of patches (Equations 39 to 41)
P	patch size (Equations 39 to 41)
P_1, P_2	concentration of a component in two types of particles
$\bar{P}$	overall or mean concentration
r	radius
r	estimate of intraclass correlation coefficient (Equation 10)
R, R^2	estimates of the relative standard deviation and relative variance due to sampling
s_s, s_s^2	estimates of standard deviation and variance due to sampling
s_a, s_a^2	estimates of standard deviation and variance due to analysis
s_o, s_o^2	estimates of overall standard deviation and variance
s_{ss+a}, s_{ss+a}^2	estimates of overall standard deviation and variance due to subsampling and analysis
s_{Sm}^2, s_{Lg}^2	estimates of variance due to sampling of small increments of weight w_{Sm} and of large increments of weight w_{Lg}
s_b^2, s_w^2	estimates of variances between randomly selected increments and within pairs of increments
$s(x_i)$	Gaussian cumulative distribution value for the ith data point in a series of data points ranked from i=1 to i=n
t	Student's t
u	linear dimensions of a cube
w	increment weight
w_{opt}	optimum increment weight
w_{Lg}, w_{Sm}	weight of large and small increments

w_1, w_2	increment weights used to produce composites of weights w_{Sm} and w_{Lg} (Equation 29)
$\bar{x}$	overall or mean concentration
x, x'	concentrations of a component in two increments collected as a pair (Equation 10)
x_1, x_2, x_3	factors in a factorial experiment (Table 2)
x_{f}	factor
x_{i}	value for the *i*th data point in a series of data points ranked from i=1 to i=n
z	degree of segregation
z	standard normal variable (Table 12 and Equation 35)
α	probability level
ν	degrees of freedom
ρ	population intraclass correlation coefficient
σ_{Sm}, σ_{Lg}	true standard deviations due to sampling of small increments of weight w_{Sm} and large increments of weight w_{Lg}
σ^2_{Sm}, σ^2_{Lg}	true variances due to sampling of small increments of weight w_{Sm} and large increments of weight w_{Lg}

LIST OF DEFINITIONS

Accuracy	The degree of agreement of a measured value with the true or expected value of the quantity of concern.
Bias	A systematic error inherent in a method or caused by some artifact or idiosyncrasy of the measurement system.
Bulk Sampling	Sampling of a material that does not consist of discrete, identifiable, constant units, but rather of arbitrary, irregular units.
Homogeneity	The degree to which a property of substance is randomly distributed throughout a material. Homogeneity depends on the size of the units under consideration. Thus a mixture of two minerals may be inhomogeneous at the molecular or atomic level but homogeneous at the particulate level.
Increment	An individual portion of material collected by a single operation of a sampling device, from parts of a lot separated in time or space. Increments may be either tested individually or combined (composited) and tested as a unit.
Individuals	Conceivable constituent parts of the population.
Laboratory sample	A sample, intended for testing or analysis, prepared from a gross sample or otherwise obtained. The laboratory sample must retain the composition of the gross sample. Often reduction in particle size is necessary in the course of reducing the quantity.
Lot	A quantity of bulk material of similar composition whose properties are under study.
Population	A generic term denoting any finite or infinite collection of individual things, objects, or events in the broadest concept; an aggregate determined by some property that distinguishes things that do and do not belong.
Precision	The degree of mutual agreement characteristic of independent measurements as the result of repeated application of the process under specified conditions.
Relative standard deviation	Standard deviation expressed as a percentage of the mean.

Relative variance	Variance expressed as a percentage of the mean.
Standard deviation	(Also called uncertainty or random error.) The mathematical value describing the precision of a measurement.
Strata	Segments of a lot that may vary with respect to the property under study.
Subsample	A portion taken from a sample. A laboratory sample may be a subsample of a gross sample; similarly, a test portion may be a subsample of a laboratory sample.
Test portion	(Also called specimen, test specimen, test unit, aliquot.) That quantity of material of proper size for measurement of the property of interest. Test portions may be taken from the gross sample directly, but often preliminary operations such as mixing or further reduction in particle size are necessary.
Variance	The square of the estimate of standard deviation. In an analytical process, variances can be defined either for distinct stages as the sampling, subsampling or analytical stages, or can be reported as a combination of those stages.

1. INTRODUCTION

The development of analytical methods to identify more compounds at ever decreasing levels is giving scientists a greater ability to collect data that will permit rational, scientifically based decisions on a variety of matters ranging from process and quality control in industry to development of policies for environmental protection. The analysis of a test sample is only one part of the overall analytical process that controls the quality of the data and therefore the appropriateness of the response. Hahn (1), Ku (2), Kratochvil and Taylor (3) and Pardue (4) have provided models for the overall process. All shared the common feature that the sampling stage of the analytical process could significantly affect the confidence that is placed in analytical data.

A review prepared by Kratochvil, Wallace and Taylor (5) in 1984 on sampling for chemical analysis suggests that many scientists are now giving the sampling stage of the analytical process the attention that it deserves. The review, which is provided as Appendix A, covers the period 1975 to 1983 and contains approximately 550 reference. A search using the keywords "sampl#" and "analy#" for the period 1983 to 1988 identified over 25,000 English-language articles in Chemical Abstracts, Biological Abstracts and American Petroleum Institute Abstracts. Of these, approximately 700 also described statistical considerations used in either planning of the analytical process or evaluation of the data. While many of the papers are specific to a single analyte within one class of population, as a set they provide invaluable background information about a myriad of sampling situations.

Four workers, Gy, Benedetti-Pichler, Ingamells, and Visman, have made especially significant contributions to general statistical sampling theory as applied to sampling for chemical composition. Each developed his ideas after years of work in the areas of geochemical or mineral evaluation.

Gy studied the sampling of granular materials from streams in mineral benefication and extraction plants (6). He proposed that the sampling of a heterogeneous material containing a small quantity of a sought-for substance depends on particle shape, particle size distribution, the composition of the phases comprising the particles, and the degree to which the sought-for substance is liberated from the remainder of the material (gangue) during particle size reduction by grinding or crushing. He defined factors f, g, c, and l to quantify these four effects.

The shape factor, f, is the ratio of the average volume of all particles having a maximum linear dimension equal to the mesh size of a screen to that of a cube which will just pass the same screen. Thus $f =$ 1.00 if all particles are cubes and 0.524 if they are all spheres. For most materials f can be assumed to be 0.5.

The particle size distribution factor, g, is the ratio of the upper size limit of the particles (screen size through which 95% of the particles pass) to the lower size limit (screen size through which 5% of the particles pass); $g = 1.00$ if all particles are the same size.

The composition factor, c, is given by

$$c = \frac{1 - \bar{x}}{\bar{x}} [(1 - \bar{x}) d_x + \bar{x} d_g] \qquad [1]$$

where $\bar{x}$ is the overall concentration of the component (mineral) of interest and d_x and d_g are densities of the component of interest and the remaining material (gangue). The value of c can range from 0.05 g/cm^3 for a high concentration of the analyte to 10^6 or greater for trace concentrations.

The liberation factor, l, is defined as the square root of the ratio of diameter of the average grains of the sought-for component in the material divided by the diameter of the largest particles in the mixture. The value of l approaches 1.00 as particle size approaches grain size.

After these four constants have been estimated, the sampling variance s_s^2 for an increment weight w can be estimated by

$$s_s^2 = fglu^3/w \qquad [2]$$

where u is the linear dimension of the largest particles. Alternatively, the sample weight required for any desired uncertainty level can be calculated.

Benedetti-Pichler considered bulk materials as two-component mixtures, with each component containing a different percentage of the analyte (7,8). The number of particles n required to hold the sampling standard deviation (sampling uncertainty) to a preselected level may be calculated from the relation

$$n = \left[\frac{d_1 d_2}{\bar{d}^2}\right]^2 \left[\frac{100(P_1 - P_2)}{R\bar{P}}\right]^2 (p)(1 - p) \qquad [3]$$

where d_1 and d_2 are the densities of the two kinds of particles, $\bar{d}$ is the average density of the sample, P_1 and P_2 are the percentage compositions of the component of interest in the two kinds of particles, $\bar{P}$ is the overall average composition in percent of the component of interest in the sample, and p and $1 - p$ are the fractions of the two kinds of particles in the bulk material. Once density, particle number, and particle size are known, the weight of sample required for a given level of relative sampling uncertainty, R, can be obtained. For example, assuming spherical particles, the minimum sample weight is given by $(4/3)\pi r^3 n\bar{d}$. Alternatively, for a specified sample weight the extent of grinding necessary to increase n to a value corresponding to any selected sampling uncertainty can be determined. If particles of varying size are present in a bulk sample, the large particles control the sampling uncertainty, and the calculations should be based on their diameter. The size of screen through which 95% of the bulk sample passes is the diameter used in the calculation. By selecting this value, the increment weight which should yield a specified sampling uncertainty is not controlled by one or two unusually coarse particles in the bulk sample.

It is apparent from the form of the Gy and Benedetti-Pichler equations that it is necessary to define the size of particles in the population of interest as well as many other properties of those particles. In its rigorous form, the Ingamells sampling constant, K_s, is subject to the same limitations (9). Ingamells derived the sampling constant expression by assuming that the sampling characteristics of a bulk material for a given component can be duplicated by considering the material to consist of a mixture of uniform cubes of two kinds of particles, one containing P_1% and the other P_2% of the component of interest. He showed that for heavy metal ores

$$K_s = 10^4 (\bar{P} - P_2)(P_1 - P_2)\ u^3 d_2/\bar{P}^2 \qquad [4]$$

where $\bar{P}$ is the overall percentage of the sought-for component in the sample, d_2 is the density of the particles continuing the highest percent P_2, of the sought-for component, and u^3 is the volume of one of the cubes.

However, the Ingamells equation can be reduced to the form

$$K_s = wR^2 \qquad [5]$$

where w is the average increment weight that yields a relative sampling standard deviation R (10). In this form the equation shows that K_s is the increment weight required to hold R to 1% relative at the 68% level of confidence. K_s can be evaluated from the relative standard deviation obtained by analyzing a set of increments of a known weight rather than knowledge of the characteristics of particles in the population of interest.

Implicit in the Gy, Benedetti-Pichler and Ingamells equations is the assumption that sampling variance is inversely proportional to increment weight. Only Ingamells clearly stated that his formula was restricted to the sampling of well-mixed materials that were free of stratification (segregation).

Visman's theory of sampling considers the effects of heterogeneity in both well-mixed and segregated populations (11). It provides the statistical foundation for collection of laboratory samples of coal as described in the American Society of Testing and Materials standard method D2234-82 (12).

Visman developed an equation

$$s_s^2 = \frac{A}{wn} + \frac{B}{n} \qquad [6]$$

that describes sampling variance, s_s^2, as the sum of random (A term) and segregation (B term) components. When values for the constants A and B

are known for a material the sampling variance for n increments, each weighing w units, can be calculated. Equation 6 was derived by calculating the sampling uncertainty as a function of increment size for 2500 lead balls on a 100 X 100 grid of sites. The balls were placed on the sites in various systematic or random patterns, samples of 1, 3 X 3, or 9 X 9 sites were collected, and the number of lead balls in each sample was recorded (3). The populations sampled included a population that was completely segregated (i.e., the degree of segregation, z, equals 1 where all the lead balls occupied adjacent sites in a corner), and populations with values of z equal to 0.33, 0.20, and 0.11. These distributions are distinguished from random distributions by the presence of patches or strata. For a fixed composition the average size of the patches increases and the number decreases with increasing segregation.

Visman's approach can be used to define the degree of segregation of a chemical substance in a bulk material. It addresses from a sampling perspective "worst case" segregation, that is, the case where the patches are themselves randomly distributed. It will result in oversampling if a trend exists in the concentration of the component through the population.

Values for the sampling constants A and B can be determined by analyzing sets of large and small increments of weights w_{Lg} and w_{Sm}. If the sizes of the increments differ sufficiently, then

$$A = \frac{w_{Lg}w_{Sm}}{w_{Lg} - w_{Sm}} (s_{Sm}^2 - s_{Lg}^2) \qquad [7]$$

$$B = s_{Lg}^2 - \frac{A}{w_{Lg}} \quad \left[\text{or } s_{Sm}^2 - \frac{A}{w_{Sm}} \right] \qquad [8]$$

and

$$z = (B/Am)^{1/2} \qquad [9]$$

where m is the reciprocal of the average particle mass of the material and has the same units of mass as A.

w_{Sm} is usually equal to the smallest test portion weight that can be analyzed with adequate precision by the method of choice. w_{Lg} usually exceeds the weight limit for a single test portion as defined by the method and usually represents the largest possible weight that permits thorough homogenization and representative subsampling.

Duncan has pointed out that the assumption implicit in Equations 7 and 8 that variance due to segregation is independent of increment size may not be true (13). Instead, the apparent degree of segregation, which can be related to the intraclass correlation coefficient for sets of samples, decreases with increasing increment size. Ensuing discussions between Visman and Duncan (14, 15) led to a second method of estimating values for A and B, applicable if an average particle mass can be obtained. In this method increments of a fixed weight are collected in sets and analyzed. For the case where increments are collected in pairs an intraclass correlation coefficient, r, may be calculated for the measurement of interest by

$$r = \frac{2\Sigma[(x - \bar{x})(x' - \bar{x})]}{\Sigma(x - \bar{x})^2 + \Sigma(x' - \bar{x})^2} \qquad [10]$$

where $\bar{x}$ is the mean of all observations and the terms x and x' are individual data points within each pair (16). Alternatively r can be calculated from within- and between-set variances, s_w^2 and s_b^2, from an analysis of variance (ANOVA) of the data. Then

$$r = (s_b^2 - s_w^2)/(s_b^2 + (n - 1)s_w^2) \qquad [11]$$

where n equals the number of increments in each set.

Equation 11 reduces to

$$r = (s_b^2 - s_w^2)/(s_b^2 + s_w^2) \qquad [12]$$

when increments are collected in pairs (i.e., $n = 2$). In cases where the number of pairs, p, is small, the value of r calculated from ANOVA data more closely approximates the rigorous expression of Equation 10 when Equation 12 is modified to

$$r = [(p - 1)s_b^2 - ps_w^2]/[(p - 1)s_b^2 + ps_w^2] \qquad [13]$$

Once the value of r is known, it may be used to calculate A and B by simultaneous solution of Equation 8 and

$$r = B/Am \qquad [14]$$

The degree of segregation, z, equals $r^{1/2}$.

Limiting values for ρ, the population intraclass correlation coefficient, are 0 and 1. The estimator, r, of ρ sometimes can have negative values. Such values are assumed to be a result of the random selection of increments and to indicate a value for ρ of zero. Under these conditions Equation 14 yields $B = 0$ and the population is considered to be well-mixed.

The major drawback to the use of r and Equation 14 is the difficulty in estimating an average particle mass. For a moderately uniform particulate mixture a value may be obtained readily by particle sizing techniques such as sieving along with knowledge of the average density of the material. But for many bulk materials, such as oil sand and soil, particles are not clearly defined, and an average particle mass cannot be measured.

The four sampling theories discussed here share the common feature that they are most applicable to sampling populations ranging in size from laboratory samples to multi-tonne bulk samples encountered in stock-piles, ships or process streams in some industries. The variables used to control sampling variance are size or number of increments or both. They assume a random assignment of sampling location or sampling at specified intervals in either time or space with a random starting point.

The theories described above have not been applied widely to routine sampling in nature such as orebody evaluations, water quality surveys in oceans, lakes and rivers or estimating biological populations. Here, pattern recognition techniques such as bootstrapping (17), calculation of fractal dimension (18), or geostatistics (19), which identifies the range of influence of samples, are more appropriate. Application of these techniques permits identification of trends within a population which can then be used to pinpoint the most appropriate sampling locations for the estimation of composition and variability. These techniques are identified here because they can be invaluable in the modelling and planning of an analytical process but they are not discussed further in this thesis.

In this research sampling theory, particularly the Visman approach to sampling of segregated materials, is advanced through sampling experiments carried out on a non-particulate material, Athabasca oil sand, and on populations generated by computer simulations. In particular the role of the particle, a fundamental unit which controls sample variability, is examined for non-particulate materials. Previously identified relations between the Visman, Gy and Ingamells constants (20) are examined and clarified. As a prerequisite to the statistical sampling evaluations of Athabasca oil sand, a subsampling method of high precision was developed and analytical precision was estimated so that precise estimates of sampling variance could be obtained.

Overall, the research project provides:

- specific recommendations for homogenizing and subsampling laboratory samples of oil sand to obtain representative 100- to 150-g test portions,
- an assessment of the nature of the distribution of the major components in bulk samples of Athabasca oil sand that are necessary for the development of sampling guidelines,
- an evaluation of existing sampling theories to the sampling of non-particulate materials, and
- a study of the applicability and limitations of sampling theory to a variety of populations.

2. THE OIL SAND SAMPLING EXPERIMENT

2.1 The Relationship Between the Physical Structure of Athabasca Oil Sand and Sample Variability

The geological history of the Athabasca deposits is a key to understanding the physical structure and therefore the difficulty in obtaining representative samples of oil sand for measurement of the major components. Depositional models for the McMurray formation sediments, the major oil bearing zones in the deposit, have been prepared (21,22).

It is generally accepted that the Athabasca oil sands were formed by deposition of sediments in marine, fluvial, estuarine and floodplain environments with subsequent lateral migration of oil into the formation. The final composition of oil sand on both the scale of the deposit (over distances of kilometres and depths of the order of many metres) and on the local scale (cm) was controlled primarily by the permeability and porosity of the sediments in the path of the migrating oil which in turn are controlled by the depositional environment of the host sediments. In zones where transport of sediments was sluggish, clay and silt were deposited. These ultimately produced shales or shaly sands which had low permeability and porosity and whose ability to accept significant amounts of oil as it migrated into place was low.

In zones occupied by river channels where currents were stronger, clays and silts tended to remain in suspension. Primarily, sand grains were deposited. These zones were relatively permeable and porous and subsequently allowed considerable amounts of oil (up to twenty percent by weight of oil sand) to enter.

The boundaries between shaly, low-grade oil sands and sandy high-grade zones are not distinct. During the process of deposition, river channels continually eroded previously deposited floodplain silts and clays. Old river channels sometimes were abandoned. Sediment supply varied. In his summary of the geology of the Athabasca oil sands Mossop concluded that "extreme lateral and vertical variability in facies is the rule rather than the exception" (23).

The description by Mossop implies that even on a local scale, significant variations in the particle size distribution and therefore the composition of Athabasca oil sand in terms of its bitumen, water and solids content can be expected. Innes and Fear (24) and Camp (25) have documented trends in the relationships between the concentration of the major components of oil sand. To summarize their work:

- Bitumen content tends to decrease with increasing water and fines (solids which pass a 44 μm sieve) content.
- Water content tends to increase with increasing fines content.
- The sum of bitumen and water contents tends to decrease with increasing fines content.

Takamura's model for Athabasca oil sand on a microscopic scale (26), reproduced in Figure 1, can be used to explain these trends. The pore spaces in the sediments were occupied by water before the oil migrated into place. During migration, the oil displaced the water from the large pores but could not displace the water from the smaller pores. The presence of fine particles effectively reduced the pore size. Pores occupied by fines therefore tended to remain saturated with water rather than become saturated with oil.

The work of Mossop, Innes and Fear, Camp and Takamura suggests that variations on the scale of the deposit down to the microscopic scale contribute to the variability of oil sand. The degree of variability has been calculated on a single core section by Shaw using a near infrared diffuse reflectance technique to measure the bitumen content of 1-cm intervals of core over a 4.27-m section (27). The bitumen content of the individual increments ranged from 0 to 18.2% with a mean and a standard deviation of 10.6 and 4.4%.

Wallace and Kratochvil's estimates of oil sand variability summarized in Table 1 (28) were considerably lower because they were measured on mined samples of oil sand which had been exposed to some degree of mixing rather than on relatively undisturbed core. In addition, the bulk samples represented a small vertical profile compared to the lateral profile which reduced the effect of the vertical variability in the deposit; also, test sample portions weighed 120 g compared to an effective test sample size of approximately 1 g in Shaw's

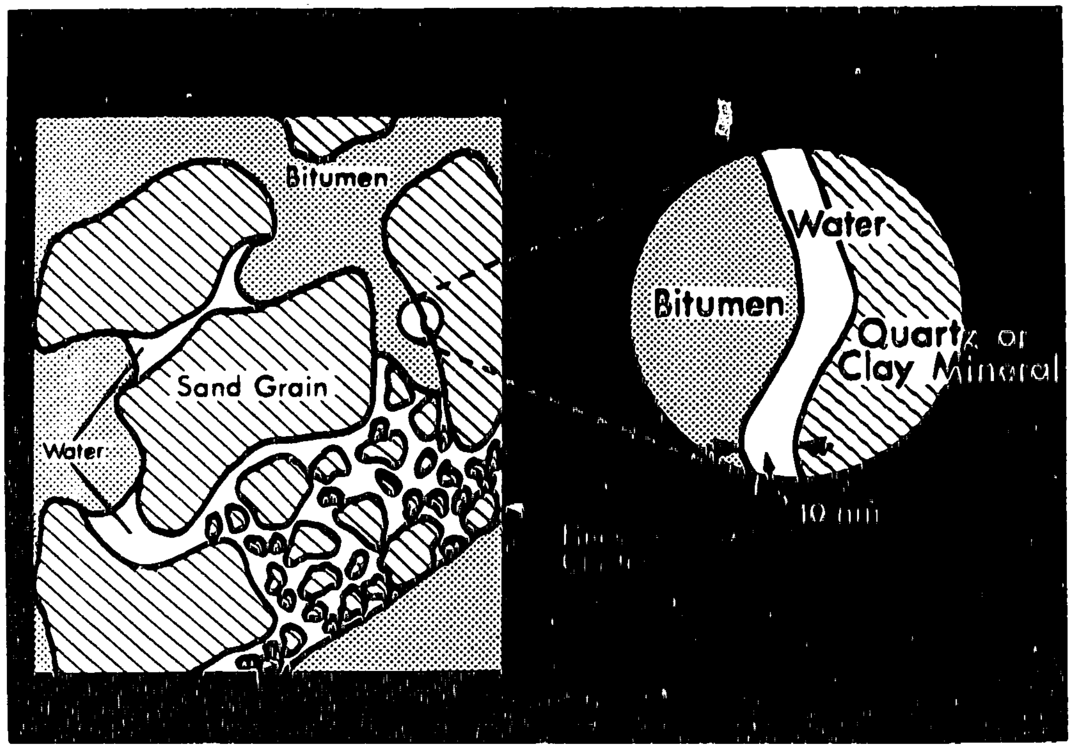


Figure 1. Schematic of the microstructure of Athabasca oil sand (26).

Table 1: Typical variability at the 120-g level of bulk samples of Athabasca oil sand (28)

Grade of oil sand and month collected		Number of analyses	Bitumen mean %	Standard deviation due to sampling (%)	Range (%)
High-grade	Nov. 76	233	14.9	0.6	12.5-16.7
	Dec. 80	80	13.8	0.8	8.9-14.9
	Nov. 81	94	14.9	1.2	9.4-17.3
Medium-grade	Nov. 76	49	11.7	0.6	3.6-12.8
	Nov. 76	49	12.2	1.2	8.7-13.9
	Dec. 80	30	12.3	1.4	8.5-14.5
	Nov. 81	15	12.3	0.4	11.5-13.3
Low-grade	Nov. 76	48	6.8	1.7	3.8-12.7
	Nov. 81	13	8.2	1.3	6.1-10.5

study. Wallace and Kratochvil's estimates of variability could be used in the planning of sampling protocols for pilot plant operations that develop extraction processes but not in orebody evaluations for commercial operations. However, their estimates were valid only for increment sizes in the 120-g range. To determine whether this size was the most efficient for reducing sampling uncertainty, estimates of variability at other increment sizes were needed.

2.2 Selection of Subsampling and Analytical Methods for Determining the Bitumen, Solids and Water Content of Oil Sand

An examination of the relationship between the uncertainty of an overall analytical operation and the uncertainty of its parts (analysis, subsampling and sampling):

$$s_o = \left(s_s^2 + s_{ss+a}^2 \right)^{1/2} \qquad [15]$$

reveals the importance of using analytical and subsampling techniques whose uncertainty, s_{ss+a} is small compared to the overall uncertainty, s_o, when determining the magnitude of the uncertainties in the sampling operation. A first order estimate of random error or uncertainty in s_s, is calculated by the method of propagation of errors (29), and is given by:

$$\Delta s_s = \left[\frac{s_o^2 \; \Delta s_o^2 + s_{ss+a}^2 \; \Delta s_{ss+a}^2}{s_o^2 - s_{ss+a}^2} \right]^{1/2} \qquad [16]$$

For the bitumen content of oil sand, s_o is typically 1% and s_{ss+a} approximately 0.10%. The 68% confidence limits in s_o for collection of approximately 50 data points, the effort used in this study to characterize the variability of oil sand, is approximately 0.05 based on χ^2 distribution statistics (28, 30) and for the purpose of this estimate, a 100% relative error in s_{ss+a} is assumed so that Δs_{ss+a} = 0.10. Substitution of these values into the equation above yields a value for Δs_s of

$$\left[\frac{1^2 \times 0.05^2 + 0.1^2 \times 0.1^2}{1^2 - 0.1^2}\right]^{1/2} = 0.05$$

which is the same as Δs_o.

In other words, if a subsampling and analytical protocol could be developed so that s_{ss+a} was 0.1% or less, the random error of subsampling and analysis would have no measurable effect on the precision of the estimate of sampling uncertainty and by extension no measurable effect on the precision of the sampling constants. This criterion is considerably more stringent than Youden's recommendation that there is little point in reducing analytical uncertainty to less than one-third of the overall uncertainty during routine analysis (31).

2.2.1 Analytical Method for Oil Sand Assays

Numerous analytical methods for measuring the concentrations of bitumen, solids and water in test portions of oil sand have been developed and evaluated. Most of the methods involve partial or complete separation of the components before measurement. An exception is the near infrared-diffuse reflectance method recently developed by Shaw (27), which had not been evaluated at the time of this study and which, from material handling considerations, would not have been appropriate for a study of bulk oil sands.

In the category of partial separations, Ball and co-workers developed a method in which test portions of oil sand are mixed with a known quantity of a solvent such as tetrahydrofuran or a blend of toluene and isopropyl alcohol (32). The dissolved bitumen is measured spectrophotometrically (33) or gravimetrically by pipetting an aliquot onto a preweighed filter paper, allowing the solvent and water to evaporate at room temperature and re-weighing the filter. The solids are washed with solvent on a filter, dried and weighed.

In the category of complete separations, the Dean-Stark solvent-extraction apparatus (34) has been modified (35) and is routinely used for oil sand assays.

For this study, a method developed by analysts in the oil sands industry that combined the best features of the Ball and Dean-Stark methods was selected. It consists of solvent extraction of bitumen and azeotropic distillation of water in the modified Dean-Stark apparatus shown in Figure 2. All components are measured gravimetrically. The "filter-paper" method is used to measure bitumen. This method offers a significant savings in time and improvement in accuracy relative to other gravimetric techniques which require rotary evaporators or forced

Figure 2. Modified Dean-Stark extraction units. The unit on the left is partially disassembled to show the cellulose thimble containing the oil sand in the neck of the extraction flask.

air ovens to remove the solvent from the extracted bitumen. The method is described in Appendix B. A brief assessment of the most probable bias errors associated with the method also is provided.

2.2.2 Prior Studies on Subsampling Laboratory Samples of Oil Sand

Procedures that yield representative test portions from laboratory samples of oil sand have not been established to the same degree as analytical methodology. Nonetheless, there are two references in the literature to this topic.

Shaw evaluated chopping, coning and quartering for the preparation of 30-g test portions of Athabasca oil sand from a 6-kg laboratory sample composed of equal parts of low-, medium- and high-grade (7, 11 and 14% bitumen) oil sands (36). This laboratory sample provided a thorough test of the effectiveness of the subsampling procedure. Shaw calculated that three coning and quartering operations resulted in subsampling uncertainties of approximately 0.5% for bitumen and solids and 0.2% for water from oil sand having an average composition of 11% bitumen, 88% solids and slightly less than 1% water. He confirmed that particle size reduction is a key to reducing subsampling uncertainty. (Here particle size refers to the size of the lumps of material produced by chopping the oil sand with a heavy knife.) He also documented systematic error caused by evaporation of water during chopping, coning and quartering. Shaw concluded that this procedure, although providing accurate results if the evaporation of water is taken into account, is too inefficient to be recommended for routine preparation of laboratory samples of oil sand for determination of oil, water and solids content. His results, however, provide excellent reference data for evaluating other subsampling techniques.

In principle, a mechanical device should yield more consistent and representative test portions from laboratory samples of oil sand than manual procedures. At ambient temperatures, however, even low levels of shear such as produced in cutting or chopping may cause separation of bitumen from sand and, therefore, increase subsampling systematic errors. But as the temperature is lowered, bitumen becomes harder and a variety of grinding methods become more feasible.

Syncrude Canada Research Ltd. has described the operation of a cryogenic grinder (Mikro-Pulverizer Model 1ST, Ducron-Mikropul Ltd., Bramalea, Ontario) for homogenizing oil sand (37) but have not published a statistical evaluation of the grinder. A potential source of bias at low temperatures is condensation of water on the oil sand leading to high results in the water analyses.

A mill developed by Quadro Engineering, Waterloo, Ontario, was used successfully by the National Research Council at low levels of shear and ambient temperatures to reduce the lumps of clay and shale in 1-ton lots of low grade oil sand and reject from the feed stream of oil sand in a commercial plant (38). On the basis of their success with the mill for particle size reduction a bench-scale model (Comil) was evaluated for subsampling laboratory samples of oil sand for analysis. Unlike many mills and blenders, the Comil does not homogenize materials; rather, it reduces the particle size of the feed to permit easier subsequent homogenization and subsampling.

2.2.3 Statistical Evaluation of the Comil-Subsampler

In the Comil the material to be reduced is gravity-fed continuously into a cone-shaped sieve constructed of approximately 1-mm stainless steel. Typical sieves are 12 cm high, 12.3 cm in diameter at the top, and 4 cm in diameter at the truncated closed bottom of the cone. Sieves with either square or round openings ranging from 0.22 mm to 19 mm are available. A variable speed, belt-driven impeller rotates within the sieve. Clearance between the sieve and the impeller is less than 1 mm. The milled material drops from the outer surface of the cone into a collection container. Preliminary trials on oil sand using a sieve with 4-mm openings indicated that the sieve openings were too small. Satisfactory milling action was obtained when the 4-mm screen was replaced by one with 12-mm square openings.

To subsample the milled material a rotating sample collection device based on the principles of a spinning riffle was designed. Spinning riffles are generally accepted as being the most suitable apparatus for subsampling batches of granular material, but oil sand would be expected to clog commercial riffles. Therefore a subsample collector was constructed from seven pie-shaped polyethylene containers each 13 cm long, 11 cm wide at the outer edge and 4 cm deep. These containers (obtained in a department store as pie-wedge savers) were mounted on a 28-cm diameter circle of 1-cm plywood and taped together along the top and bottom edges to prevent oil sand from falling between the compartments. The assembly was then mounted on a vertical axle and driven by a laboratory stirrer through a rubber stopper on the stirrer drive shaft and positioned against the edge of the circular wooden platform. The complete mill and subsampler assembly is shown in Figure 3. A velocity of 80 rpm was found to be the maximum that could be used without loss of oil sand from centrifugal force.

Although precision in the size of the individual subsamples is not critical, in twenty-one tests on various grades of Athabasca oil sand the relative standard deviation in the weights of the seven subsamples was typically 5% for mean subsample weights of 135 g. A ranking test showed that at the 95% level of confidence none of the compartments in the subsampler collected subsamples that were consistently lighter or heavier than the other subsamples. This data plus other raw data collected during the evaluation of the mill and spinning riffle are provided in Appendix C.

In seven tests, the lightest and heaviest subsamples were analyzed but no significant bias in composition was apparent (see Appendix C). Average differences of only 0.1% in the bitumen, water and solids contents were found.

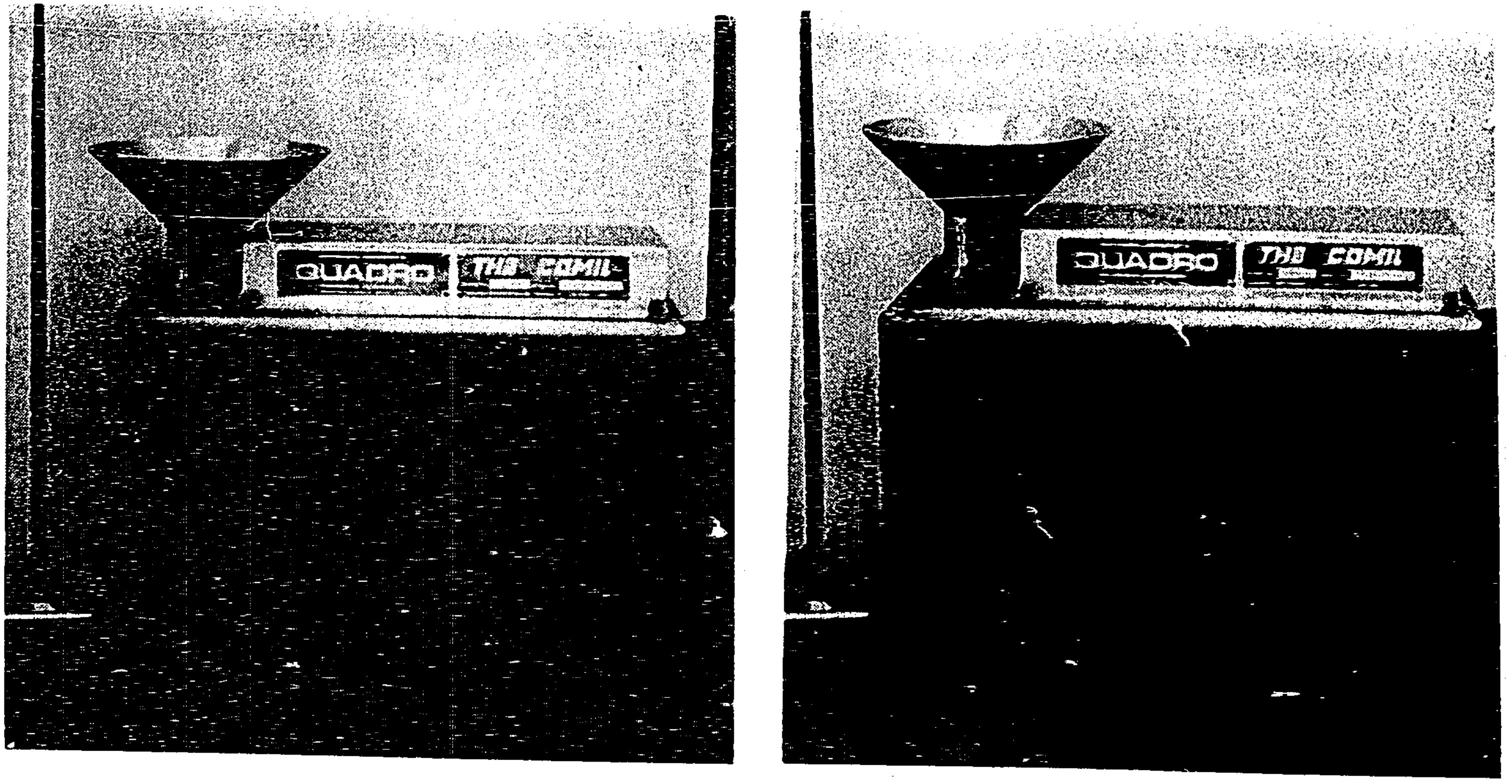


Figure 3. The Comil-subsampler for obtaining test portions of oil sand. In the photograph on the right, the sleeve which directs the oil sand into the spinning subsampler has been removed to show the sieve. In both photographs, the drive system for the subsampler is in the lower left corner.

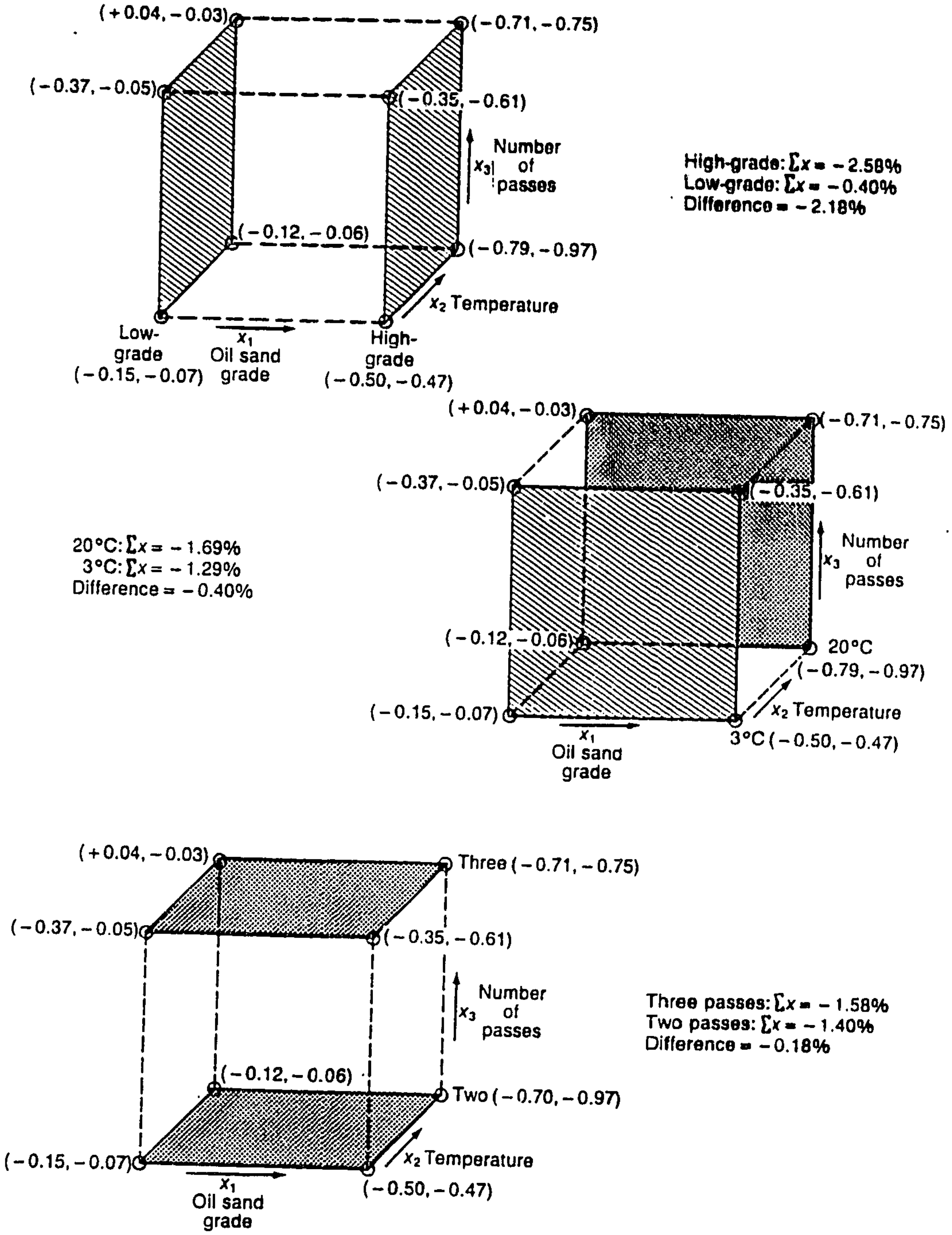
During initial studies of the mill it was observed that even when the impeller was rotated at the slowest possible speed some separation of bitumen from the sand grains occurred. Clean sand grains were present in the milled material, and small quantities of bitumen accumulated on the sieve and impeller. The problem decreased if the temperature of the oil sand feed was lowered. With frozen oil sand, however, the mill tended to jam on lumps of clay. Cooling the oil sand to about 3°C before passage through the mill, and cooling the sieve and impeller of the mill by placing dry ice in the sieve assembly for two to three minutes before the oil sand sample was introduced, provided optimum conditions. (Minor modifications to the Comil have since been reported by Quadro Engineering that permit delivery of cryogens on a continuous basis to the mill, but the modified unit was not studied in this work.) At these temperatures the clay lumps are not frozen, water condensation is not so severe a problem as at lower temperatures, and separation of bitumen from sand by the mill is reduced. During these trials, often it was found that firm lumps of oil sand and clay formed balls during the milling process; these lumps rotated within the mill rather than pass through the sieve. To mill and subsample the total laboratory sample it was necessary to break up the lumps, which weighed up to 30 g, manually and pass the total sample through the mill a second time. The problems of bitumen-sand separation and lump formation increased in severity with increasing bitumen concentration.

To determine the effects of temperature reduction and number of passes through the mill on homogeneity of low- and high- grade oil sands, a full two-level factorial experiment was conducted. This style of experiment is appropriate when factors in a test may interact and when experimental error in the response may be sizeable (39).

In a factorial experiment the significance of varying a factor is determined by comparing the average of the results from all experiments in which the level of the factor is maximized with the results in which the level is minimized. For this study, in which only three factors were examined, the experiment can be represented as a cube, as shown in Figure 4. The effect of changing a factor is the mean difference between the results on the opposite faces of the cube.

In the statistical analysis the significance of the effect is determined with the repeatabilities of the experiments taken into account. Table 2, using data from Figure 4, provides an example of such a calculation. When data in the columns show an effect greater than the minimum significant effect, the factors or interactions associated with those columns can be considered to be significant.

Eight 1-kg laboratory samples of a high-grade Athabasca oil sand (14% bitumen) and eight of a low-grade Athabasca oil sand (9% bitumen) were milled under the conditions listed in Table 3. Duplicate runs were made for each set of conditions in random order so that the significance of each factor could be determined.



High-grade: $\sum x = -2.58\%$
Low-grade: $\sum x = -0.40\%$
Difference = -2.18%

20°C: $\sum x = -1.69\%$
3°C: $\sum x = -1.29\%$
Difference = -0.40%

Three passes: $\sum x = -1.58\%$
Two passes: $\sum x = -1.40\%$
Difference = -0.18%

Figure 4. Depiction of a three-factor, two-level factorial experiment. The data superimposed on the figure is the bias in the estimate of bitumen content as a function of operating conditions of the Comil.

Table 2: Effect of operating conditions on maximum bias in % bitumen estimate for both high- and low-grade oil sands[(a)]

Trial	Mean	Factors[(a)]			Interactions				Maximum bias (from Table 4)		$\bar{x}$	s
		x_1	x_2	x_3	x_1x_2	x_1x_3	x_2x_3	$x_1x_2x_3$	T-1	T-2		
1	+	-	+	-	-	+	-	+	-0.12	-0.06	-0.09	0.04
2	+	+	+	-	+	-	-	-	-0.79	-0.97	-0.88	0.13
3	+	-	-	-	+	+	+	-	-0.15	-0.07	-0.11	0.06
4	+	+	-	-	-	-	+	+	-0.50	-0.47	-0.49	0.02
5	+	-	+	+	-	-	+	-	+0.04	-0.03	+0.01	0.05
6	+	+	+	+	+	+	+	+	-0.71	-0.75	-0.73	0.03
7	+	-	-	+	+	-	-	+	-0.37	-0.05	-0.21	0.23
8	+	+	-	+	-	+	-	-	-0.35	-0.61	-0.48	0.18
Sum+	-2.98	-2.58	-1.69	-1.58	-1.93	-1.41	-1.32	-1.52				
Sum-	0.00	-0.40	-1.29	-1.40	-1.05	-1.57	-1.66	-1.46		s_{pooled} = 0.12		
Diff.	-2.98	-2.18	-0.40	-0.18	-0.88	0.16	0.34	-0.06				
Effect[(b)]	-0.37	-0.55	-0.10	-0.06	-0.22	0.04	0.09	-0.02				

(a) In this table, the factors entitled x_1, x_2 and x_3, refer to the grade of oil sand, the temperature of the oil sand feed, and the number of passes through the mill. the "+" and "-" signs describe the factor levels; "+" means high-grade oil sand, 20°C and 3 passes while "-" means low-grade oil sand, 3°C and 2 passes.

(b) Minimum significant effect at 95% confidence = $ts\ (2/mk)^{1/2}$ (where m = number of trials/2 and k = number of replicates per trial)

$$= 2.31 \times 0.12 \times (2/4 \times 2)^{1/2}$$
$$= 0.14$$

at 90% confidence $= 1.86 \times 0.12 \times (2/4 \times 2)^{1/2}$

$$= 0.11$$

The sixteen laboratory samples were taken with minimum disturbance from sealed 1-gallon containers of Athabasca oil sand mined from Suncor's lease in the Athabasca deposit in July 1979 and stored at room temperature (20°C) until the time of use, October 1982. Eight were then placed in a refrigerator at 3°C and eight on the bench overnight to meet the temperature specifications of the factorial experiment. The samples were then milled through the 12-mm square sieve in the Comil at the slowest impeller speed (approximately 60 rpm). The speed of the spinning subsampler was 80 rpm for all runs. The sieve and impeller were cooled with dry ice prior to milling of the 3°C samples. The seven subsamples produced from each run were transferred into glass 120-mL Boston round bottles and the bottles sealed until analysis.

The weight of each subsample was recorded for later comparison with the weight of the original laboratory sample (1.000 kg). After each run, the sieve was thoroughly washed with toluene and the washings saved in a glass bottle for analysis. Any stones in the oil sand which did not pass the sieve were weighed and discarded. Four randomly selected subsamples out of the seven produced from each run, along with the toluene washings, were analyzed by the modified Dean-Stark method to determine the bitumen, solids, and water contents.

The average composition and variability of the four subsamples analyzed from each run are given in Table 3 with individual results for the test samples provided in Appendix C. The initial response variables to assess the performance of the mill were the fraction of oil sand held

Table 3: Conditions and a summary of analytical results from a full-factorial experiment to evaluate the Comil-spinning subsampler for bitumen, solids, and water analysis of two grades of oil sand[(a)]

Condition (trial) number	Factor			% Bitumen	% Solids	% Water
	Grade of oil sand	Temperature of oil sand feed	Number of passes through mill			
1	Low	20°C	2	8.89±0.11	86.94±0.17	3.96±0.15
				10.85±0.27	86.50±0.22	2.27±0.09
2	High	20°C	2	14.08±0.05	80.30±0.13	5.25±0.19
				13.19±0.05	84.12±0.19	2.39±0.17
3	Low	3°C	2	9.71±0.08	85.35±0.15	4.59±0.19
				8.29±0.11	86.85±0.11	4.55±0.18
4	High	3°C	2	13.75±0.05	82.81±0.09	3.10±0.12
				13.80±0.13	82.45±0.12	3.42±0.10
5	Low	20°C	3	8.76±0.08	85.42±0.06	5.53±0.13
				9.63±0.16	86.53±0.16	3.56±0.09
6	High	20°C	3	13.94±0.07	81.15±0.16	4.54±0.11
				13.33±0.08	84.41±0.07	1.96±0.03
7	Low	3°C	3	8.90±0.06	86.05±0.13	4.80±0.09
				9.32±0.11	86.67±0.08	3.76±0.16
8	High	3°C	3	13.78±0.08	82.20±0.13	3.74±0.19
				13.51±0.05	82.92±0.18	3.19±0.25

(a) Each analytical result is the average and standard deviation from the analysis of four test samples.

up in the mill and the maximum bias introduced by holdup of bitumen on the sieve.

The calculations used to determine the maximum bias and the values of the biases for each run are given in Table 4. The calculations assume that all of the material not recovered in the sample collector had the same composition as the residue retained on the sieve. This assumption neglects a small loss of oil sand (approximately 20 g) during transfer as well as some selective loss of water due to evaporation. As will be seen later, the experimental bias introduced by the milling was found to be about half the bias values calculated in Table 4. Nevertheless, calculations of this kind are useful in providing an upper limit of the level of bias that could be introduced by the mill.

The statistical significance of the retention of oil sand in the mill was determined using the calculations shown in Table 5. They show that the losses when milling high-grade oil sand are greater at the 90% level of confidence than losses when milling low-grade oil sand. In Table 2 the significance of the bias in the bitumen data is determined. The average bias in the bitumen data is 0.55% greater for high grade than for low-grade oil sand. Because an average difference of 0.14% is significant at the 95% level of confidence, the two grades of oil sand can be said to behave differently in the mill. This is supported by the presence of an x_1x_2 (grade of oil sand-temperature) interaction significant at the 80% level of confidence. The interaction implies that the magnitude of the error in the estimate of bitumen in high-grade

Table 4: Calculations of maximum bias caused by retention of bitumen in the mill

Trial	Oil sand recovered (%) (a)				Toluene washings (%)			Corrected composition (%) (b)			Bias (%) (c)		
	Weight (g)	Bitumen	Solids	Water	Bitumen	Solids	Water	Bitumen	Solids	Water	Bitumen	Solids	Water
1A	969	8.89	86.94	3.96	12.70	86.93	0.37	9.01	86.94	3.85	-0.12	0.00	+0.11
1B	969	10.58	86.83	2.21	12.46	86.89	0.65	10.64	86.83	2.16	-0.06	0.00	+0.05
2A	921	14.08	80.30	5.25	24.13	73.73	2.15	14.87	79.78	5.00	-0.79	+0.52	+0.25
2B	901	13.19	84.12	2.39	22.99	75.51	1.50	14.16	83.27	2.30	-0.97	+0.85	+0.09
3A	944	9.63	85.47	4.55	12.33	86.72	0.94	9.78	85.54	4.35	-0.15	-0.07	+0.20
3B	957	8.29	86.85	4.55	10.03	89.72	0.25	8.36	86.97	4.36	-0.07	-0.12	+0.19
4A	948	13.75	82.81	3.10	23.39	74.64	1.96	14.25	82.38	3.04	-0.50	+0.43	+0.06
4B	939	13.80	82.45	3.42	21.49	76.93	1.58	14.27	82.11	3.31	-0.47	+0.34	+0.11
5A	958	8.17	86.41	5.15	8.98	90.83	0.19	8.20	86.60	4.94	-0.03	-0.19	+0.21
5B	927	9.59	86.59	3.54	9.02	90.10	0.90	9.55	86.85	3.35	+0.04	-0.26	+0.19
6A	921	13.94	81.15	4.45	22.92	74.43	2.65	14.65	80.62	4.30	-0.71	+0.47	+0.15
6B	937	13.33	84.41	1.96	25.29	73.22	1.49	14.08	83.71	1.93	-0.75	+0.70	+0.03
7A	901	8.86	86.11	4.78	12.62	86.64	0.75	9.23	86.16	4.38	-0.37	-0.05	+0.40
7B	960	9.14	86.93	3.69	10.37	88.65	0.98	9.19	87.00	3.58	-0.05	-0.07	+0.11
8A	931	13.78	82.20	3.74	18.82	80.23	0.94	14.13	82.07	3.55	-0.35	+0.13	+0.19
8B	939	13.51	82.92	3.19	23.56	75.50	0.94	14.12	82.47	3.05	-0.61	+0.45	+0.14

(a) Weight of oil sand recovered equals the total weight of the seven subsamples collected after milling. Composition has been corrected for stones in the oil sand.

(b) Weight of recovered oil sand x % of component + weight of sample not recovered x % of that component in toluene washings/1000 g. The weight of sample not recovered equals 1000 g, the original weight of the laboratory sample, minus the weight of oil sand recovered.

(c) Experimental mean value - corrected composition.

Table 5: Effect of operating conditions on the percentage of feed oil sand recovered.

Trial	Mean	Factors[(a)]			Interactions				% Oil sand recovered (from Table 4)		$\bar{x}$	s
		x_1	x_2	x_3	x_1x_2	x_1x_3	x_2x_3	$x_1x_2x_3$	T-1	T-2		
1	+	-	+	-	-	+	-	+	96.9	96.9	96.9	0.00
2	+	+	+	-	+	-	-	-	92.1	90.1	91.1	1.41
3	+	-	-	-	+	+	+	-	94.4	95.7	95.1	0.92
4	+	+	-	-	-	-	+	+	94.8	93.9	94.4	0.64
5	+	-	+	+	-	-	+	-	95.8	92.7	94.3	2.19
6	+	+	+	+	+	+	+	+	93.7	92.1	92.9	1.13
7	+	-	-	+	+	-	-	+	90.1	96.0	93.1	4.17
8	+	+	-	+	-	+	-	-	93.9	93.1	93.5	0.57
Sum+	751.3	371.9	375.2	373.8	372.2	378.4	376.7	377.3			s_{pooled} =	1.84
Sum-	0	379.4	376.1	377.5	379.1	372.9	374.6	374.0				
Diff.	751.3	-7.5	-0.9	-3.7	-6.9	5.5	2.1	3.3				
Effect[(b)]	93.9	-1.9	-0.2	-0.9	-1.7	1.4	0.5	0.8				

(a) In this table, the factors entitled x_1, x_2 and x_3, refer to the grade of oil sand, the temperature of the oil sand feed, and the number of passes through the mill. the "+" and "-" signs describe the factor levels; "+" means high-grade oil sand, 20°C and 3 passes while "-" means low-grade oil sand, 3°C and 2 passes.

(b) Minimum significant effect at 95% confidence = 2.1; at 90% confidence = 1.7; at 80% confidence = 1.4.

oil sand is increased at higher temperatures. Further statistical evaluations of the effect of temperature and the number of times a sample was run through the mill were performed separately for the two grades of oil sand.

The evaluations identifying the effect of operating conditions on the maximum bias in the estimates of % solids and % water as well as on the ranges of bitumen, solids and water contents found for the four test samples of oil sand from each experiment are given in Appendix C. Neither the temperature of the mill and sample nor the extent of milling significantly affected the range of results found within each set of four test samples. The spinning subsampler obviously collected repeatable samples independent of the operating conditions of the mill.

The results in Tables 6 and 7 indicate that for both low- and high-grade oil sands no improvement in precision results from passing a sample through the mill more than two times. They also show that the temperature of the mill and sample does not significantly affect the bitumen content of the low-grade oil sand which passes through the mill. However, systematic errors in the estimation of bitumen content are reduced significantly by milling high-grade oil sands at lower temperatures.

Even when milling high-grade oil sands at low temperatures, a measurable bias remains. The average loss of material through retention on the sieve, holdup in the mill, and loss during handling for high-

Table 6: Effect of operating conditions on the maximum bias in the estimate of % bitumen estimate in low-grade oil sand

Trial	Mean	x_2	x_3	x_2x_3	Maximum bias (from Table 4) T-1	T-2	Mean	Standard deviation
1	+	-	-	+	-0.12	-0.06	-0.09	0.04
3	+	+	-	-	-0.15	-0.07	-0.11	0.06
5	+	-	+	-	0.04	-0.03	-0.01	0.05
7	+	+	+	+	-0.37	-0.05	-0.21	0.23
Sum+	-0.40	-0.32	-0.20	-0.30			s_{pooled}	= 0.12
Sum-	0.00	-0.08	-0.70	-0.10				
Diff.	-0.40	-0.24	0.00	-0.20				
Effect[(b)]	-0.10	-0.12	0.00	-0.10				

(a) Descriptions of the symbols and variables are provided in Table 3.

(b) Minimum significant effect,

$$[\text{min}]_{95\%\ \text{confidence}} = ts\ (2/mk)^{1/2}$$
$$= 2.78 \times 0.12 \times (2/(2\times2))^{1/2}$$
$$= 0.24$$
$$[\text{min}]_{90\%\ \text{confidence}} = 2.13 \times 0.12 \times (2/(2\times2))^{1/2}$$
$$= 0.18$$

Table 7: Effect of operating conditions on maximum bias in the estimate of % bitumen in high-grade oil sand [(a)]

Trial	Mean	x_2	x_3	x_2x_3	Maximum bias (from Table 4) T-1	T-2	Mean	Standard deviation
1	+	+	-	-	-0.79	-0.97	-0.88	0.13
3	+	-	-	+	-0.50	-0.47	-0.49	0.02
5	+	+	+	+	-0.71	-0.75	-0.73	0.03
7	+	-	+	-	-0.35	-0.61	-0.48	0.18
Sum+	-2.58	-1.61	-1.21	-1.22			s_{pooled}	= 0.11
Sum-	0.00	-0.97	-1.37	-1.36				
Diff.	-2.58	-0.64	0.16	0.14				
Effect[(b)]	-0.65	-0.32	0.08	0.07				

(a) Descriptions of the symbols and variables are provided in Table 3.

(b) Minimum significant effect at 95% confidence = 0.21;
at 90% confidence = 0.17.

grade oil sand run under refrigerated conditions was 56 g out of 1000 (5.6%). The average composition of the material retained on the sieve was 22.9% bitumen, 75.9% solids and 1.2% water. The amount of material lost during subsampling is independent of sample size; therefore the maximum bias in analysis would increase as the size of the laboratory sample decreased. Figure 5 provides estimates for the bias that could be expected in bitumen, water, and solids data when subsampling quantities of high grade oil sand (14% bitumen, 3% water and 83% solids) from 500 to 1000 g. The lower limit was chosen arbitrarily and the upper limit was the limit of the mill-subsampler as set up for this study.

An example of the calculations employed to determine the points in Figure 5 follows. A 500 g sample of oil sand containing 14.0% (70 g) bitumen is milled and subsampled. During the process 56 g of material is lost. This material contains 22.9% bitumen, based on the average composition of the toluene washings (a worst-case scenario), and so a maximum of 12.8 g of bitumen is lost. The remaining 57.2 g of bitumen remains in the 444 g of recovered material. Therefore the recovered oil sand would have a measured bitumen content of 12.88%. From these values the maximum bias in bitumen content expected for a 500 g sample of this oil sand would be -1.12%.

Figure 5 illustrates that the bias expected in the subsampling of high grade oil sand is minimized by adjusting the size of the laboratory sample to as near the capacity of the spinning riffle as possible.

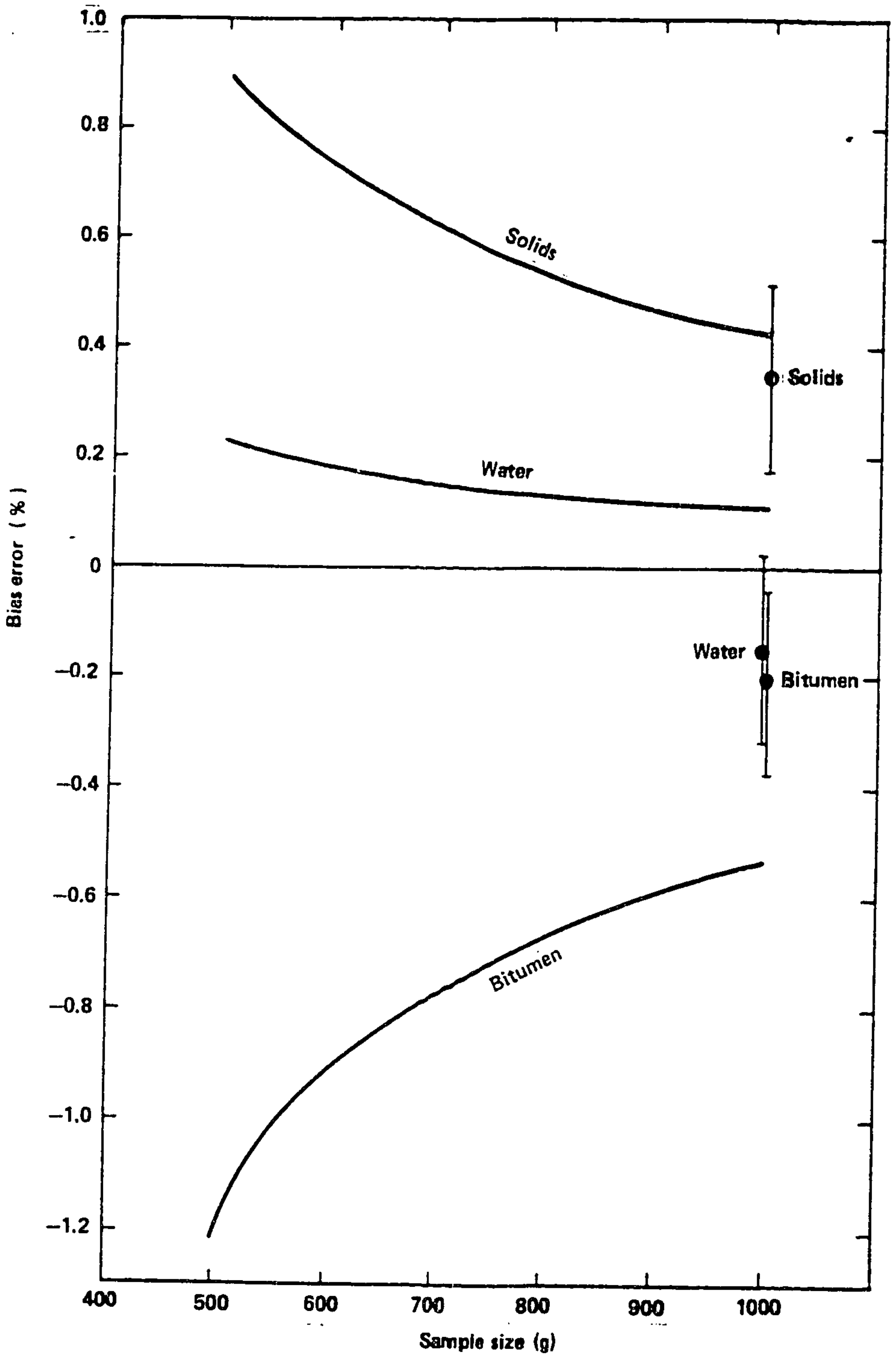


Figure 5. Relationships between bias and weight of a laboratory sample of high-grade oil sand.

Figure 5 and Table 4 also indicate that subsampled oil sand contains more water than the original oil sand. This contradicts historical data indicating that water is lost during subsampling. These calculations were based upon the assumption that there was no evaporation of water from either the residue on the sieve or from the subsamples themselves. In fact, evaporation did occur, as was shown by the following experiment.

Five 5-kg samples of a high-grade oil sand, collected from the lower bench in the Suncor mine in 1981, were homogenized by kneading in plastic bags. A 1-kg test portion was taken from each sample and analyzed in large Dean-Stark extractors. A second 1-kg test portion was taken from each sample and milled, under refrigerated conditions, by the procedure described before. All of the oil sand recovered from the mill was analyzed. Table 8 provides a summary of the results. In all sets some evaporation occurred during milling and handling, giving an average systematic error of 0.2% absolute low in the determination of water in the oil sand. Thus evaporative loss of water will introduce a negative bias, that is, the measured water content will be less than the true water content. Since the magnitude of the negative bias caused by water loss will depend on variables such as time of exposure, surface area, and relative humidity, it cannot be evaluated with precision. Water loss from the oil sand would also have a net effect of increasing the magnitude of the systematic error in the determination of solids and decreasing it for the determination of bitumen.

Table 8: Direct evaluation of bias caused by milling high grade oil sand

Component	Trial					Mean	Standard deviation
	1	2	3	4	5		
Bitumen (wt.%)							
Milled	14.81	13.25	15.51	12.79	14.46	14.16	1.12
Original	14.96	13.53	15.76	12.65	14.71	14.32	1.23
Difference	-0.15	-0.28	-0.25	+0.14	-0.25	-0.16	0.17
Solids (wt.%)							
Milled	81.78	83.37	83.33	81.36	83.01	82.57	0.94
Original	81.41	83.10	82.96	81.24	82.42	82.23	0.86
Difference	0.37	0.27	0.37	0.12	0.59	0.34	0.17
Water (wt.%)							
Milled	2.87	3.16	0.87	5.63	2.32	2.97	1.73
Original	3.09	3.25	0.96	5.99	2.54	3.16	1.82
Difference	-0.22	-0.09	-0.09	-0.36	-0.22	-0.19	0.11

The errors reported in Table 4 for the solids and water are smaller by about a factor of two than the maximum possible error because the oil-rich residue on the screen usually accounted for only about half of the lost oil sand. The remaining half was the result of hang-up in other parts of the mill and loss of material during transfer. Such material would on average be more representative of the oil sand. Precise estimation of the error is not possible owing to variations in the clay content of the oil sand; the presence of clay and shale tends to clean bitumen from the sieve.

For low-grade oil sand, systematic errors directly attributable to the mill are much smaller and less sensitive to sample size than for high-grade oil sand because retention of oil sand on the screen is a minor problem, and because with low-grade feed the composition of the retained oil sand is more similar to that of the original. Low-grade oil sands contain on average more water, so the problem of water loss from these materials generally is considered to be more severe. Although the extent of the problem was not studied in this work, bias errors for water as a function of water content of high-grade samples, summarized in Table 8, confirm this suspicion. A correlation coefficient of less than 0.81 (40) indicates no correlation at the 90% level of confidence between the amount of water lost and the amount of water in the oil sand. The calculated correlation coefficient of 0.82 slightly exceeds this value.

To confirm that two passes at 3°C are adequate for a variety of oil sands, additional 1-kg oil sand samples were subsampled. The results, reported in Table 9, confirm that the observations in the factorial experiments hold true for a variety of oil sand compositions.

The analysis of several test portions from each run afforded an opportunity to define estimates of precision for the subsampling and analytical operations on 1-kg laboratory samples of oil sand. Estimates of precision were prepared separately for oil sands containing greater than and less than 12% bitumen by weight. This division point was chosen arbitrarily on the basis of observed differences in the ability of the mill to reduce various grades of oil sands. The values determined by pooling the standard deviations in Tables 3 and 9 are summarized in Table 10. The similarities in precision estimates for the high- and low-grade oil sands further confirm the proficiency of the subsampler even though a variable systematic error is introduced by the mill.

2.2.4 Conclusions about the Comil-Subsampler

1. This evaluation demonstrated that the Comil-spinning riffle assembly can be used to obtain repeatable test portions of oil sand from 1-kg increments taken from bulk samples of oil sand. Because the subsampling plus analytical uncertainties (random error) for a single bitumen, solids or water determination for both low- and high-grade oil sand were in the range of 0.10 to 0.14 percent absolute, they would have no effect on the precision of the

Table 9: Subsampling errors for a variety of oil sands

	Mean composition (%) ± standard deviation of 4 subsamples			Maximum bias (%)[a]		
	Bitumen	Solids	Water	Bitumen	Solids	Water
High-grade oil sand	13.34±0.05	84.52±0.03	1.71±0.05	-0.44	+0.40	+0.03
High-grade oil sand	14.60±0.24	84.40±0.23	0.56±0.06	-0.40	+0.38	0.00
Medium-grade oil sand	10.38±0.08	84.82±0.13	4.31±0.15	-0.06	-0.01	+0.06
Low-grade oil sand	7.75±0.17	85.79±0.12	5.99±0.08	-0.09	-0.05	+0.13
Conditioning drum oversize	6.05±0.10	91.45±0.10	2.18±0.10	0.00	0.00	0.00

(a) Maximum bias was calculated by the method shown in Table 4.

Table 10: Precision and accuracy statements for subsampling and analysis of high- and low-grade Athabasca oil sands

	High-grade oil sand[a] precision (s_{ss+a})	High-grade oil sand bias[c] (absolute %)	Low-grade oil sand[b] precision (s_{ss+a})	Low-grade oil sand bias[d] (absolute %)
Bitumen	0.10	-0.2	0.13	0.0
Solids	0.14	0.3	0.14	0.3
Water	0.14	-0.2	0.13	-0.3

(a) >12% bitumen, no clay or shale; average water content of 3% assumed.

(b) <12% bitumen or >12% bitumen with visible clay and shale lenses.

(c) Measured value - true value for data reported in Table 4.

(d) Accuracy of the solids and bitumen based upon 50% of the maximum possible bias calculated from the data for low-grade oil sand in Table 8 and adjusted for evaporation of water. Average water content of 6% assumed.

sampling uncertainties and sampling constants calculated for bulk samples of Athabasca oil sand. (Although this study was limited to a maximum size of 1 kg per laboratory sample, the mill without the subsampler has since been used by the author for particle-size reduction of up to 20-kg samples. The milled oil sand, after being tumbled in plastic bags, typically exhibits a variability of ±0.2%.)

2. Some separation of bitumen from sand grains does occur during milling, although not to the degree found in a centrifugal grinding mill[a] which had been found in preliminary work to cause almost complete separation of bitumen from the sand. To reduce separation and the accompanying bias due to selective retention in the mill of a material rich in bitumen, samples should be cooled to approximately 3°C prior to milling. The mill should be cooled with dry ice and the size of the laboratory sample should be kept as large as the equipment will permit to minimize systematic error. Samples of oil sand should be passed through the mill twice to reduce lumps. Repeatability of the subsampling operation is not improved by more than two passes.

3. Evaporation of water during subsampling is the major contributor to systematic error in the estimates of the water (-0.3%) and solids

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[a] Centrifugal Grinding Mill ZM-1; Brinkmann Instruments Inc., 50 Galaxy Blvd., Rexdale, Ontario, M9W 4Y5.

(+0.3%) in low-grade oil sand. The estimate of bitumen is almost free of systematic error. Loss of water is also a problem in the subsampling of high-grade oil sand. Separation of bitumen from the sand grains and selective retention of a bitumen-rich material on the sieve of the mill also contribute to the systematic error for sands containing >12% bitumen; this additional error is of the order of -0.2% for bitumen and water and +0.3% for solids.

3. EVALUATION OF STATISTICAL SAMPLING METHODS FOR ATHABASCA OIL SAND

3.1 Background

In previous work carried out to determine sample variability in bulk samples of Athabasca oil sand, values for sampling constants calculated by three approaches had been estimated for nine lots of oil sand (28). All were based on variability determined for 120-g increment sizes.

In the first approach, the minimum number of samples n required to stay within prespecified limits of confidence and standard deviation was determined using the equation derived from classical statistics:

$$n = \frac{t^2 s_s^{\,2}}{R^2 \bar{x}^2} \times 10^4 \qquad [17]$$

Here t is the Student's t-table value for the desired level of confidence, R is the percent relative standard deviation acceptable in the average, and $s_s^{\,2}$ and $\bar{x}$ are estimates of the variance and average concentration of a component in a bulk sample (3). Application of this equation involves setting t at a value corresponding to $n = \infty$ at the desired confidence limits, obtaining a preliminary value for n, substituting the t value for this n, and iterating to constant n.

The number of increments required to hold the sampling uncertainty to 5% relative within 95% confidence limits ranged from 2 to 96 for bitumen, from 3 to 15 for solids and from 45 to over 300 for water.

Alternatively, the acceptable sampling error was defined relative to the analytical error. The overall variance of a series of determinations is a sum of the variances in each sampling stage and the analysis of the test portion as described by

$$s_o^2 = s_a^2 + s_s^2 \qquad [15]$$

If the sampling standard deviation s_s is three times the analytical standard deviation s_a, further reduction in s_a has negligible effect on the overall standard deviation s_o (31). In other words, when $s_a = 0.15$, the overall variance, s_o, must be less than $(.15)^2 + (3 \times .15)^2 = 0.2250$ for s_a to have any significant contribution to s_o.

When the analytical and sampling variances are known, the number of samples required to reduce the overall variance to a specified level can be calculated from the equation

$$s_o^2 = \frac{s_s^2}{i} + \frac{s_a^2}{ij} \qquad [18]$$

where i is the number of increments collected and j the number of replicate analyses per increment (41).

If only a single determination is conducted per sample ($j = 1$), Equation 18 can be rearranged to give the minimum number of increments collected and analyzed so the overall uncertainty contains no significant contribution from the measurement error by

$$i = \frac{s_s^2 + 0.0225}{0.225}$$

For all three components, i as defined above, fell in the range of 10.

Finally, the Ingamells' sampling constant approach was also used. K_s is defined as the size of a single subsample to be taken from a well-mixed material to ensure a subsampling standard deviation no greater than 1% relative within 68% confidence limits. The relation is:

$$K_s = wR^2 = w(100s_s/\bar{x})^2 \qquad [5]$$

where w is the average subsample weight giving a relative standard deviation, R, in percent. For well-mixed materials K_s is independent of the size of subsamples analyzed to determine it value. For increment weights of 120g, wR^2 varied from 1,300 to 32,000 g for bitumen, 60 to 390 g for solids and 34,000 to 250,000 g for water. Clearly the lots were heterogeneous, and this heterogeneity is a major contributor to the uncertainty in analytical measurements of composition.

In this chapter, the effect of varying the size of increments, taken directly from lots of Athabasca oil sand, on sampling uncertainty is examined. Use of larger initial portions or increments should reduce the contribution of sampling to the overall uncertainty in reported results from sampling operations. Questions addressed are: What descriptors suitably estimate the variability of bulk samples of mined Athabasca oil sand? What level of sampling is required to hold sampling uncertainty to a level sometimes required in pilot-scale processes in the oil sands industry (1% relative is chosen as the most stringent probable requirement.)?

3.2 Experimental

Two samples of oil sand, a high-grade sand containing 12 to 15% bitumen and a low-grade sand containing 8 to 10% bitumen, were taken by front-end loader in October 1982 from the upper mining bench in the Suncor mine of the Athabasca deposit near Fort McMurray, Alberta. The oil sand was off-loaded into metal drums (46-Imperial gallon) lined with polyethylene and transported to storage at -15°C within 12 hours. Sampling was conducted about a month after collection.

One day before sampling, one drum of each grade was taken from cold storage and the oil sand allowed to thaw. A total of 195 increments were collected from each drum by coring. Cores were obtained by inserting plastic tubes 15 cm long and 7 cm I.D., with 2-mm walls, into the sand as shown in Figure 6. One layer of the drum comprised 39 cores; five layers were collected. The operation was performed so as to minimize disturbance of the oil sand. The ends of each core were covered first with thin polyethylene film (Saran Wrap) and then with aluminum foil held in place by fiberglass tape. The cores, each of which contained about 950 g of oil sand, were then stored upright in a freezer at -15°C labelled in the manner shown in Figure 6.

For the work described here, 48 cores randomly selected from each drum were placed in a refrigerator at about 3°C one day prior to subsampling. Reduction and subsampling operations to obtain a 130-g test portion from each core were carried out using a mechanical mill and spinning subsampler as described in Chapter 2. A second set of 48 cores from each drum were selected randomly, allowed to thaw, and cored axially with a number 15 cork borer to produce test portions approximately 2 cm in diameter by 15 cm long and weighing about 50 g. The 50 and 130-g test portions were analyzed for bitumen, water and solids by the modified Dean-Stark method described in Appendix B. A third set of 48 cores was selected as before and allowed to thaw. Each was halved longitudinally to produce ~500-g test portions which were analyzed in scaled-up modified Dean-Stark extractors.

Because early rounding may lead to significant errors, all calculations were carried using five significant figures and were rounded at the end.

3.3 Results and Discussions

The assays of all the samples collected are given in Appendices D

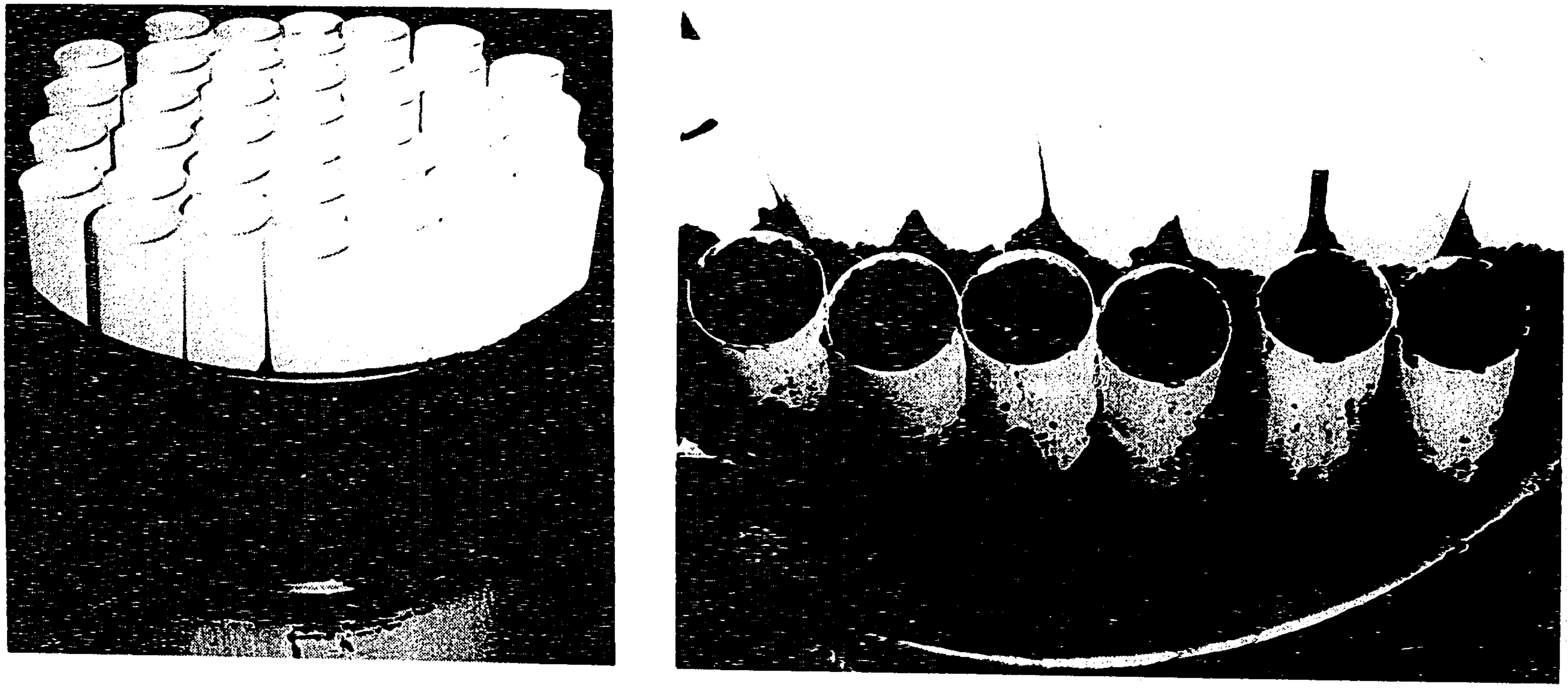

Figure 6. Coring of drums of oil sand. The left photograph shows the pattern of core tubes in the drum. Each core was labelled by a designation *a-b-c* where *a* equalled either 1 (high-grade) or 2 (low-grade) oil sand, *b* referred to the level from which the core was taken from the drum (i.e. 1 to 5) and *c* was the lateral location of the core on each level as shown in this figure. On each level, the core numbers began at number 1 in the upper left corner, number 5 in the upper end of the second row from the left and proceeded in this manner to number 39 in the lower right corner. In the right photograph, two rows of cores have been removed. The fourth row will be inserted to their full depth before the third row is removed.

and E with a summary of results provided in Table 11. Here the standard deviation due to sampling has been calculated by the relation:

$$s_s = \left(s_o^2 - s_{ss+a}^2\right)^{1/2} \qquad [19]$$

where s_o is the standard deviation of the 48 values in each data set and s_{ss+a} is the standard deviation of the subsampling and analytical operations. Values for s_{ss+a} for the largest laboratory samples were determined in separate experiments by analyzing two test portions collected during the reduction and subsampling of twelve laboratory samples each of the high-grade and low-grade oil sands. The results of the individual analyses used to calculate s_{ss+a} are given in Appendix D and a summary of the estimated values of s_{ss+a} is provided in Table 11. Although described as s_{ss+a} in Table 11, for the 500- and 50-g samples, that uncertainty is due solely to analytical error and is assigned an average value as estimated by Shaw (27). He had estimated the weighing and measurement errors in each stage of the assay and derived the analytical uncertainty using the method of propagation of errors. Individual results of the tests used to calculate sampling constants for oil sand are given in Appendix E. To ensure that Gaussian statistics were in fact appropriate to describe the variability of the major components in Athabasca oil sand, the numerical Kolmogorov test (42) was carried out. A sample calculation using the data for bitumen content of 952-g increments from the high-grade oil sand is provided in Table 12.

Table 11: Sampling uncertainties for determination of bitumen, solids and water in two grades of oil sand. Each average is based on 48 determinations.$^{(a)}$

	High-grade oil sand Increment weight			Low-grade oil sand Increment weight		
	952 g	501 g	50.3 g	952 g	500 g	50.6 g
Bitumen						
$\bar{x}$	14.31	14.32	13.95	8.51	8.62	8.16
s_o	1.00	0.94	1.86	0.70	0.94	1.32
s_{ss+a}	0.19	0.05	0.05	0.08	0.05	0.05
s_s	0.98	0.94	1.86	0.70	0.94	1.32
Solids						
$\bar{x}$	83.87	83.65	83.30	85.77	85.76	85.54
s_o	0.53	0.50	0.74	1.01	1.06	1.40
s_{ss+a}	0.19	0.05	0.05	0.11	0.05	0.05
s_s	0.49	0.50	0.74	1.00	1.06	1.40
Water						
$\bar{x}$	1.38	1.85	2.10	5.27	5.38	5.71
s_o	0.69	0.71	1.44	1.42	1.46	2.00
s_{ss+a}	0.10	0.05	0.05	0.10	0.05	0.05
s_s	0.68	0.71	1.44	1.42	1.46	2.00

(a) s_o = overall standard deviation, s_{ss+a} = standard deviation of subsampling and measurement operations, and s_s = standard deviation of the sampling operation.

In this test, the data are arranged in ascending order from $i = 1$ to n and the difference $x_i - \bar{x}$ for each increment calculated. The difference between the actual cumulative distribution value and theoretical Gaussian cumulative distribution value for n data points is calculated as shown in Table 12. If the largest value of D_i exceeds standard tabular values by the amount also shown in Table 12, the distribution can be considered as non-Gaussian.

Table 13 is a summary of the maximum values of D_i calculated for the three components in both bulk samples of oil sand. Because the critical value for D equals 0.196 for a set of 48 data points at the 95% level of confidence and no D_i values exceeded this level, it was concluded that all data sets generated in this sampling experiment could be treated using Gaussian statistics.

In Table 14, single sampling constants based on the relation of Ingamells are summarized. The data show that the sampling constants calculated in this manner depend on sample size and that segregation is therefore present. This result was also observed on evaluation of data from measurements on 120- and 5000-g samples collected at the Alberta Research Council from 1979 to 1984 (43) and summarized in Table 15.

Because of dependence on sample size, single sampling constants as described in Chapter 1 are only appropriate for predicting the level of

Table 12: Kolmogorov's test for normality - % bitumen in large samples of high grade oil sand

x_i	$x_i-\bar{x}$	i	i/n	$s(x_i)$	$\lvert D_i \rvert$
11.91	-2.40	1	.021	.008	.013
12.28	-2.03	2	.042	.021	.021
12.33	-1.98	3	.063	.023	.040
12.60	-1.71	4	.083	.043	.040
12.71	-1.60	5	.104	.054	.050
13.36	-0.95	6	.125	.171	.016
13.54	-0.77	7	.146	.221	.075
13.60	-0.71	8	.167	.239	.072
13.63	-0.68	9	.188	.248	.060
13.68	-0.63	10	.208	.264	.056
13.75	-0.56	11	.229	.288	.059
13.76	-0.55	12	.250	.291	.041
13.77	-0.54	13	.271	.295	.024
13.82	-0.49	14	.292	.312	.020
13.86	-0.45	15	.313	.326	.013
13.86	-0.45	16	.333	.326	.007
13.97	-0.34	17	.354	.367	.013
14.05	-0.26	18	.375	.397	.022
14.08	-0.23	19	.396	.409	.013
14.10	-0.21	20	.417	.417	.000
14.14	-0.17	21	.438	.432	.006
14.14	-0.17	22	.458	.432	.026
14.18	-0.13	23	.479	.448	.031
14.20	-0.11	24	.500	.456	.044
14.21	-0.10	25	.521	.460	.061
14.30	-0.01	26	.542	.496	.046
14.37	-0.06	27	.563	.524	.039
14.39	0.08	28	.583	.532	.052
14.44	0.13	29	.604	.552	.052
14.46	0.15	30	.625	.560	.065
14.52	0.21	31	.645	.583	.062
14.60	0.29	32	.667	.614	.053
14.88	0.57	33	.688	.716	.028
14.89	0.58	34	.708	.719	.011
14.91	0.60	35	.729	.726	.003
14.95	0.64	36	.750	.739	.011
15.11	0.80	37	.771	.788	.017
15.18	0.87	38	.792	.808	.016
15.19	0.88	39	.813	.811	.002
15.27	0.96	40	.833	.832	.001
15.30	0.99	41	.854	.839	.015
15.51	1.20	42	.875	.887	.012

Table 12: (Continued)

x_i	$x_i - \bar{x}$	i	i/n	$s(x_i)$	$\lvert D_i \rvert$
15.53	1.22	43	.896	.891	.005
15.59	1.28	44	.917	.902	.015
15.76	1.45	45	.938	.927	.011
15.86	1.55	46	.958	.941	.017
16.07	1.76	47	.979	.962	.017
16.45	2.24	48	1.000	.984	.016

$\bar{x}$ = 14.31
s = 0.995
Maximum Value for $|D_i|$ = 0.075

x_i = Individual data points arranged in ascending order
i = Sequential data points (cumulative number of data points)
n = Total number of data points
$s(x_i)$ = Normal cumulative distribution value taken from tables for values of standard normal variables

$$z = \frac{x_i - \bar{x}}{s}$$

$$z = \frac{11.91 - 14.31}{0.995}$$

$$= 2.41 \quad \text{for } i = 1$$

$$s(x_i) = 1 - 0.992$$
$$= 0.008$$

$$|D_i| = |s(x_i) - i/n|$$

If the maximum value for $|D_i|$ is greater than D, the distribution cannot be considered as normal with a probability level α.
For α = 95%, $D = 1.36 / \sqrt{n}$
$= 0.196$ when $n = 48$.

Table 13: Kolmogorov's test for normality - a summary of maximum values of D_i determined for sampling data

	Low-grade oil sand	High-grade oil sand
Bitumen		
950 g	0.075	0.049
500 g	0.080	0.098
50 g	0.104	0.109
Solids		
950 g	0.077	0.168
500 g	0.081	0.128
50 g	0.114	0.148
Water		
950 g	0.109	0.156
500 g	0.137	0.156
50 g	0.196	0.097

At the 95% level of confidence if the maximum value of $D_i > 1.36/\sqrt{n}$ (0.196 for 48 data points), the distribution can be considered as not Gaussian. All of the data sets were considered to be Gaussian.

Table 14: Calculation of single sampling constants based on cores taken from drums of two grades of oil sand. The composite weights are calculated from Equation [5].

	Average increment weight (g)	Composite weight (g)		
		Bitumen	Solids	Water
High-grade oil sand	952	4.5×10^4	3.2×10^2	2.3×10^6
	501	2.2×10^4	1.8×10^2	7.4×10^5
	50.3	9.0×10^3	4.0×10^1	2.4×10^5
Low-grade oil sand	952	6.4×10^4	1.3×10^3	6.9×10^5
	500	6.0×10^4	7.6×10^2	3.7×10^5
	50.6	1.3×10^4	1.4×10^2	6.2×10^4

Table 15: Calculation of single sampling constants for lots of oil sand of varying grades. The composite weights are calculated from Equation [5].

Component	Composite weight (g)	
	120-g Increments [28] (a)	5000-g Increments [43] (b)
Bitumen	1.3×10^3 to 3.2×10^4	4.6×10^4 to 8×10^5
Solids	60 to 390	1.5×10^3 to 1.2×10^4
Water	3.4×10^4 to 2.5×20^5	7×10^5 to 6.2×10^6

(a) The range represents nine lots of oil sand.

(b) The range represents four lots of oil sand.

sampling for lots of oil sand if the increment size used in the determination of s_s is also used in all subsequent sampling operations. Unlike Ingamells' sampling constant, which provides the weight of a single subsample from a well-mixed population yielding a relative uncertainty of 1%, for segregated populations single sampling constants provide the weight of a composite prepared from increments weighing the same as those from which the constant was calculated. Thus for segregated or stratified materials such as oil sand, an approach that takes this additional variable into account is necessary. Visman's theory of sampling considers stratification as well as the random distribution of a component in a population as described in Chapter 1 by the equation:

$$s_s^2 = \frac{A}{wn} + \frac{B}{n} \qquad [6]$$

Recall that values for A and B can be calculated from the variances for two increment sizes by:

$$A = w_{Lg} w_{Sm} (s_{Sm}^2 - s_{Lg}^2)/(w_{Lg} - w_{Sm}) \qquad [7]$$

$$B = s_{Lg}^2 - A/w_{Lg} \qquad [8]$$

where w_{Lg} and w_{Sm} are the average weights of the large and small increments (11).

In this work three sizes of increments were analyzed. Values of A and B for the three possible pairs of data sets: 950 g and 50 g, 500 g and 50 g, and 950 g and 500 g, are shown in Table 16. The 950-500 g combination yields the least precise estimates of A and B because the

Table 16: Values for Visman's *A* and *B* sampling constants calculated for bitumen, water and solids in high- and low-grade oil sands.(a) Each value is based on $n = 48$.

Increment size pairs	High-grade oil sand			Low-grade oil sand		
	Bitumen	Solids	Water	Bitumen	Solids	Water
$A = w_{Lg} w_{Sm} (s^2_{Sm} - s^2_{Lg})/(w_{Lg} - w_{Sm})$						
952 and 500 g	0	10	411	415	130	122
952 and 50.3 g	134	16	86	67	51	105
500 and 50.3 g	144	17	88	48	47	105
$B = s^2_{Lg} - A/w_{Lg}$						
952 and 500 g	0.96	0.23	0.42	0.05	0.86	1.89
952 and 50.6 g	0.82	0.22	0.37	0.42	0.95	2.02
500 and 50.6 g	0.60	0.22	0.33	0.79	1.03	1.92

(a) Because composition is expressed in % rather than in weight fraction, A has units of g-$\%^2$ and B, $\%^2$.

ratio w_{Lg}/w_{Sm} is smallest. For example, although s_s calculated for bitumen content at the 952-g increment size was 0.98, the upper limit of the 95% confidence interval is 1.24 based on χ^2 distribution statistics. If σ_s at the 952-g level were 0.98, for a well-mixed material σ_s at the 500-g level would be 1.35, (i.e. $(0.98^2 \times 950/500)^{1/2}$) a value which falls only slightly outside the upper confidence limit for the larger increment size. Clearly, the ratio w_{Lg}/w_{Sm} for calculating the Visman constants must be much larger than two. This issue will be addressed further in Chapter 4.

Table 17, columns 3 to 5, lists the number of increments required to hold the sampling uncertainty to 1% relative, as calculated using Visman's constants from Table 16. Increasing the increment weight from 500 g to 950 g generally causes little reduction in the required number of increments. This is illustrated by the following example.

For the low-grade oil sand the data for bitumen from the 950- and 50-g increments yield values for A and B of 67.0 g%^{2} and 0.42%^{2}. Therefore, $s_s^2 = 67.0/wn + 0.42/n$. For the 500-g increments, $s_s^2 = 0.134/n + 0.42/n = 0.554/n$. The random distribution of bitumen in the oil sand therefore contributes 24% of the overall sampling variance. For the 950-g increments $s_s^2 = 0.071/n + 0.42/n = 0.491/n$, and random

Table 17: Number of increments of various sizes required to hold sampling uncertainty in two lots of oil sand to 1% relative, calculated on the basis of Visman's equation (numbers rounded to two significant figures).

Average increment weight, w_{av}(g)	Mean of 48 detns. (%)	n_{Lg-Md}	n_{Lg-Sm}	n_{Md-Sm}	$\frac{K_{s(950)}}{w_{av}}$	$\frac{K_{s(500)}}{w_{av}}$	$\frac{K_{s(50)}}{w_{av}}$
High-grade oil sand							
Bitumen	14.3						
952		47	47	37	47	23	9
501		47	53	43	89	43	18
50.3		47	170	170	890	430	180
Solids	83.9						
952		1	1	1	1	1	1
501		1	1	1	1	1	1
50.3		1	1	1	7	4	1
Water	1.4						
952		2400	2400	2200	2400	780	250
501		2600	2800	2600	4700	1700	470
50.3		6600	11000	11000	46000	17000	4700
Low-grade oil sand							
Bitumen	8.5						
952		67	68	120	68	63	14
500		120	77	120	130	120	26
50.6		1200	240	240	1300	1200	260
Solids	85.8						
952		1	1	1	1	1	1
500		2	1	2	3	2	1
50.6		5	3	3	26	15	3
Water	5.3						
952		720	760	720	720	390	65
500		760	790	760	1400	730	120
50.6		1500	1500	1400	14000	7300	1200

distribution contributes 14% of the overall sampling variance. Because the material is partially segregated, and because variance due to segregation is relatively unaffected by increment size, doubling the increment weight reduces the overall sampling variance by only 10%. If the material were well-mixed (no segregation), a reduction of 50% in the variance would have occurred. The benefit of increasing the size of the increment for a material in which segregation is present depends on both the degree of segregation of the material, and on the proximity of the size of the increment to its optimum weight w_{opt}, which is equal to A/B. If increments of optimum weight are collected, the random and segregation components contribute equally to the sampling variance regardless of the number taken as shown by:

$$s_s^2 = \frac{A}{wn} + \frac{B}{n} = \frac{A}{w_{\mathrm{opt}}n} + \frac{B}{n} = \frac{A}{\frac{An}{B}} + \frac{B}{n} = \frac{B}{n} + \frac{B}{n} \qquad [20]$$

The greatest benefit of increasing increment size occurs when the initial value is approximately w_{opt}. As increment size increases beyond w_{opt} the reduction in sampling variance with increasing size becomes smaller. The largest value for w_{opt} in Table 18 (omitting the imprecise values for the large-medium combination of measurements), is 267 g. Therefore, only a small benefit is observed on increasing w from 500 g to 950 g.

Values for single sampling constants, based on the relation of Ingamells, for 120-g and 5000-g increments are also given in Table 18.

Table 18: Optimum increment weights, w_{opt}, and single sampling constants for sampling two lots of Athabasca oil sand

	High-grade oil sand			Low-grade oil sand		
	Bitumen	Solids	Water	Bitumen	Solids	Water
w_{opt} (g) = A/B						
Large-medium$^{(a)}$	0	43	411	8300	151	65
Large-small	163	73	232	160	54	52
Medium-small	240	77	267	61	46	55
Single sampling constant values						
$K_{s(120)}$	$1.1\text{x}10^4$	$6.2\text{x}10^1$	$3.2\text{x}10^5$	$1.8\text{x}10^4$	$2.3\text{x}10^2$	$1.2\text{x}10^5$
$K_{s(5000)}$	$1.8\text{x}10^5$	$3.4\text{x}10^3$	$4.6\text{x}10^6$	$4.2\text{x}10^5$	$6.9\text{x}10^3$	$3.4\text{x}10^6$

(a) Values for w_{opt} calculated from the data sets describing the large-medium (950-500 g) samples are imprecise owing to uncertainties in estimates of A and B.

These data show, for example, that if a single composite sample is collected to estimate the bitumen content of high-grade oil sand within 1% relative at the 68% level of confidence, it would need to weigh 1.1 x 10^4 g if composed of 120-g increments or 1.8 x 10^5 g if composed of 5000-g increments. Because the values for $K_{s(120)}$ and $K_{s(5000)}$ reported for the two lots of oil sand in Table 18 generally fall within the range of the values reported in Table 15 for thirteen other lots of oil sand, we conclude that the Visman constants, A and B, calculated in this work are representative of most mined Athabasca oil sands.

Values of $K_{s(120)}$ in Table 18 were estimated by first determining the sampling variance, s_s^2, associated with collection of a single 120-g increment by substituting $n = 1$ and the appropriate sampling constants from Table 16 into Equation 6. Values for s_s^2 and $w = 120$ were then used to determine $K_{s(120)}$ by Equation 5. The values for $K_{s(5000)}$ were calculated similarly.

As the number of random sample increments n is increased the number of strata from which increments are taken is also increased, and so more representative samples can be prepared from considerably less material. In Table 17, columns 6 to 8 give the number of 950-g, 500-g and 50-g increments required to hold the sampling uncertainty to 1% relative as calculated from Ingamells' single constant K_s. The number of increments represented by K_s is obtained by dividing K_s by the increment weight.

Note that $K_{s(950)}/950$, $K_{s(500)}/500$, and $K_{s(50)}/50$ equal the number of 950-g, 500-g and 50-g increments calculated from Visman's constants. However, if $K_{s(950)}$ is used to predict the number of 500-g or 50-g increments which will hold the sampling uncertainty to 1% relative, the estimate is high. Conversely, if $K_{s(50)}$ is used to predict the number of 500-g or 950-g increments the estimate is low, because there is more benefit to increasing n than w when sampling a segregated population, owing to:

$$\frac{A}{w(x_f n)} + \frac{B}{x_f n} < \frac{A}{(x_f w)n} + \frac{B}{n} \qquad [21]$$

when x_f is greater than one.

Although the theoretical model of Athabasca oil sand developed by Takamura (26) can be invoked to explain the variability of oil sand and therefore the large number or size of increments to collect a "representative" sample, sampling theory alone also predicts the need for large increment weights. Recall that a second method of estimating Visman's sampling constants involves the analysis of pairs of increments of a weight w, calculation of an intraclass correlation coefficient r from an equation such as:

$$r = [(p-1)s_b^2 - ps_w^2]/[(p-1)s_b^2 + ps_w^2] \qquad [13]$$

where p is the number of pairs of increments and s_b^2 and s_w^2 are the between-set and within-set variances estimated from an analysis of variance, and simultaneous solution of the equations:

$$s_S^2 = \frac{A}{w} + B \qquad [6]$$

for $n = 1$

and $$r = \frac{B}{Am} \qquad [14]$$

where m is the reciprocal of particle mass (13, 14, 15).

In this work, through random selection of 48 increments of each size from the 195 possible sampling locations from each bulk sample of oil sand, several pairs of near neighbors of each increment size were selected and analyzed. These data, given in Appendix F, permitted several estimates of r to be made. At the same time, the collection of different increment sizes resulted in several estimates of A and B to be made as summarized in Table 16. Substitution of these values into Equation 14 would yield an estimate of m and from this, an average particle mass could be calculated.

A value for r was calculated initially by the rigorous equation:

$$r = \frac{2\Sigma(x - \bar{x})\ (x' - \bar{x})}{\Sigma(x - \bar{x})^2 + \Sigma(x' - \bar{x})^2} \qquad [10]$$

where x, x' are the individual results within a pair and $\bar{x}$ is the overall mean of all pairs (16), but as shown in Table 19 for a selected data set, the ANOVA method provided an almost identical estimate of the intraclass correlation coefficient.

Table 19: Comparison of three methods used to calculate an intraclass correlation coefficient for % bitumen in the high-grade oil sand

Pair	% Bitumen				
	x	x'	$(x-\bar{x})$	$(x'-\bar{x})$	$(x-\bar{x})(x'-\bar{x})$
1-1-4, 1-1-9	13.36	13.60	-0.89	-0.65	0.5785
1-1-17, 1-1-18	14.08	15.19	-0.17	0.94	-0.1598
1-1-20, 1-1-27	14.14	13.68	-0.11	-0.57	0.0627
1-1-32, 1-1-33	14.37	14.89	0.12	0.64	0.0768
1-2-12, 1-2-18	15.27	14.30	1.02	0.05	0.0510
1-3-1, 1-3-2	14.52	13.97	0.27	-0.28	-0.0756
1-3-5, 1-3-11	13.76	14.95	-0.49	0.70	-0.3430
1-3-7, 1-3-8	16.07	16.45	1.82	2.20	4.0040
1-3-17, 1-3-18	15.51	13.86	1.26	-0.39	-0.4914
1-3-26, 1-3-27	11.91	12.33	-2.34	-1.92	4.4928
1-4-12, 1-4-13	13.63	15.18	-0.62	0.93	-0.5766
1-4-26, 1-4-32	12.28	14.91	-1.97	0.66	-1.3002
1-4-21, 1-4-27	15.76	12.60	1.51	-1.65	-2.4915

Calculation of intraclass coefficient r

METHOD 1

$\bar{x} = 14.25$ $\Sigma\ (x-\bar{x})^2 + (x'-\bar{x})^2 = 34.4349$

$\Sigma\ (x-\bar{x})\ (x'-\bar{x}) = 3.8277$

$$r = \frac{2\ \Sigma\ (x-\bar{x})\ (x'-\bar{x})}{\Sigma\ (x-\bar{x})^2 + \Sigma\ (x'-\bar{x})^2} = \frac{2 \times 3.8277}{34.4349} = 0.222$$

METHOD 2 (Analysis of variance)

Variance due to	DF	SS	MS=SS/DF	F-Ratio
Between pairs (s_b^2)	12	21.04	1.75	1.70
Within pairs (s_w^2)	13	13.39	1.03	
Total	25	34.43		

$r = (s_b^2-s_w^2)/(s_b^2+s_w^2) = 1.75 - 1.03/1.75 + 1.03 = 0.259$

METHOD 3
Using the ANOVA as above but $r = [(p-1)s_b^2 - ps_w^2]/[(p-1)s_b^2 + ps_w^2] = 0.221$

In Table 20, the intraclass coefficients calculated for each component at the three increment weights collected from the high- and low-grade oil sands are considered with the estimates of A and B to calculate average particle mass. The theoretical particle mass, $1/m$, fell in the range of 20 g. Therefore, the roughly 15,000-g composite of oil sand required to hold R to 1% for a bitumen determination consists of approximately 750 "theoretical particles".

This conclusion was confirmed by means of the Benedetti-Pichler equation (7):

$$n = \left[\frac{d_1 d_2}{\bar{d}^2} \right]^2 \left[\frac{100(P_1 - P_2)}{R\bar{P}} \right]^2 p(1 - p) \qquad [3]$$

Here n is the number of particles in a mixture of two kinds of particles that must be collected to hold R to a specified level. The terms d_1, d_2, and $\bar{d}$ represent the densities of the individual kinds of particles and their average density. P_1, P_2, and $\bar{P}$ are the concentrations of the sought-for component in each kind of particle and the average concentration, while p represents the probability of finding any one kind of particle.

If an average theoretical particle of oil sand were to weigh 20 g, there would be little to distinguish between the two kinds of particles in the mixture. Then $d_1 \sim d_2 \sim \bar{d} = 2.0$ g/cm^3 and $p = 0.5$. For an oil sand with an average bitumen content $\bar{P}$ of 8%

Table 20. Estimation of average particle mass of Athabasca oil sand

	r	A	B	Average particle mass (g) $1/m = Ar/B$		z
			High-grade oil sand			
Bitumen						
950 g	0.222 (0.226)	134	0.82	36		0.470
		144	0.60	53		
500 g	0.129	134	0.82	21	Mean = 28	0.359
		144	0.60	31		
50 g	0.069	134	0.82	11		0.262
		144	0.60	17		
Solids						
950 g	0.208 (0.220)	16.4	0.22	16		0.456
		16.6	0.22	16		
500 g	0.084	16.4	0.22	6	Mean = 15	0.289
		16.6	0.22	6		
50 g	0.312	16.4	0.22	23		0.559
		16.6	0.22	24		
Water						
950 g	0.123 (0.123)	86.1	0.37	29		0.350
		87.8	0.33	33		
500 g	0.023	86.1	0.37	5	Mean = 12	0.151
		87.8	0.33	6		
50 g	-0.157	86.1	0.37	0		0.000
		87.8	0.33	0		
			Low-grade oil sand			
Bitumen						
950 g	0.215 (0.218)	67.0	0.42	34		0.463
		48.4	0.79	13		
500 g	0.085	67.0	0.42	14	Mean = 11	0.297
		48.4	0.79	5		
50 g	0.185	67.0	0.42	0		0.430
		48.4	0.79	0		
Solids						
950 g	0.393 (0.394)	51.3	0.95	21		0.627
		47.1	1.03	18		
500 g	0.800	51.3	0.95	43	Mean = 27	0.894
		47.1	1.03	37		
50 g	0.432	51.3	0.95	23		0.657
		47.1	1.03	20		
Water						
950 g	0.353 (0.353)	105	2.02	18		0.594
		105	1.92	19		
500 g	0.652	105	2.02	34	Mean = 21	0.807
		105	1.92	36		
50 g	0.147	105	2.02	8		0.383
		105	1.92	8		

$$n = 750 = \left[\frac{2 \times 2}{2^2}\right]^2 \left[\frac{100(P_1 - P_2)}{1 \times 8}\right]^2 (0.5)(0.5)$$

and the difference in composition between the two kinds of particles, $P_1 - P_2$, is approximately 4.5% - a reasonable value.

On the other hand if the average particle mass of the whole oil sand is assumed to equal the mass of an average-sized grain of silica and the sample is a mixture of particles of bitumen and silica, the values substituted into the Benedetti-Pichler equation would be as follows: d_1 (density of bitumen), 1.00 g/mL; d_2 (density of silica), 2.6 g/mL; $\bar{d}$ (density of oil sand), 2.0 g/mL; $\bar{P}$ (average concentration of bitumen in oil sand), 8%; $P_1 - P_2$, 100% - 0% = 100%. A 200-µm diameter particle of silica weighs approximately 11 µg; therefore a 15,000-g composite required to hold R to 1% would contain approximately 1.4×10^9 particles. Under these conditions

$$p(1 - p) = \frac{1.4 \times 10^9}{\left[\frac{1 \times 2.6}{2}\right]^2 \left[\frac{100 \times 100}{1 \times 8}\right]^2} = 530$$

Because $p(1 - p)$ cannot exceed 0.25, the conditions as described are theoretically impossible and the hypothesis that the average size of oil sand equals the average particle size of a sand grain must be rejected.

With the average theoretical particle mass defined, it is easy to understand why sample variability at the 50-g increment size is so large. After all, this size represents two to three particles, a number which is much too small to be very representative of any large bulk sample.

The estimates of the intraclass correlation coefficient exhibit a large degree of scatter because of the relatively small number of pairs of increments analyzed. Nevertheless, there are sufficient estimates to show that the bulk oil sand sample is highly segregated as defined by the degree of segregation, z (or $r^{1/2}$). The estimates of segregation are much higher than would be predicted if values of A and B had been estimated by the two-increment size approach and a sand-grain mass arbitrarily substituted for 1/m or if z was defined as $(B/A)^{1/2}$ which Visman proposed for materials in which the component of interest is not in clearly identifiable units.

3.4 Conclusions

1. Visman's equation allows calculation of optimum sample increment number and size for a segregated population. Increments in the range of 50 to 250 g are optimum for determination of bitumen, solids and water in mined Athabasca oil sand. Reduction of sampling uncertainty to 1% relative for either high- or low-grade oil sand requires collection of less than ten increments for solids, of the order of 100 for bitumen and of the order of 1000 for water.

2. Both segregation and local heterogeneity contribute to the need for a large number of increments to obtain a representative composite sample of Athabasca oil sand. Methods involving single constants only can be used validly to represent the weight of a composite prepared from increments of the same size as those used to calculate the constant. If larger increments are taken the constant will give a low value for the number required; if small increments are taken a high value is obtained.

3. The degree to which oversampling or undersampling will occur as a result of extrapolating from a single sampling constant, depends on the degree of segregation of the population and proximity of the chosen increment weight to the optimum increment weight, the weight at which random distribution and segregation of the component of interest contribute equally to sampling variance. In the case of Athabasca oil sand, segregation is present to a large enough degree that increasing increment weights above approximately 500 g has little effect on sampling variance.

4. An average particle mass of approximately 20 g for Athabasca oil sand explains in a purely statistical framework, the large variability at small increment sizes. This mass does not correspond to any physical structure within the oil sand. Thus for materials that do not have a definitive particulate structure it is wiser to use the two-increment-size approach for calculating A and B rather than risk choosing a wrong value for m in the intraclass correlation coefficient method.

4. THE DESIGN OF SAMPLING PLANS FOR CHEMICAL ANALYSIS OF SEGREGATED BULK MATERIALS

4.1 Background

The data reported in the previous chapters have defined sampling constants that describe the variability of bitumen, water and solids in Athabasca oil sand and have alluded to some mathematical relations between the Ingamells and Visman constants. Of particular importance was the identification of a theoretical particle as defined by sampling statistics which does not correspond to a clearly identifiable physical unit in the bulk oil sand. The experience gained in the definition of Visman's sampling constants for Athabasca oil sand provides a framework for discussion of the process by which those constants are estimated and the application of the major existing sampling theories to bulk sampling.

4.2 Guidelines for Estimating Visman's Sampling Constants

4.2.1 Two Increment-Size Approach

Given sampling constants for one or two bulk samples of a material, a person faced with developing a sampling protocol for another lot or shipment of the same material logically should question the validity of the constants for that new lot. Only after repeated sampling trials will the sampler become confident that the sampling constants represent the "typical" population of bulk samples that will be encountered. Given that there will exist differences in variability between bulk samples, there is usually little point in developing precise sampling constants for any single lot. Sampling constants generally should be considered as first-order estimates, subject to ongoing review. But the question "How many and what size of increments should be collected to provide useful estimates of the Visman sampling constants?" still remains to be addressed.

When Visman's original method is used to calculate A and B, increment size (w_{Lg} and w_{Sm}) and the number of increments in each set controls the precision of A and B. First consider increment size. The ratio $w_{\mathrm{Lg}}/w_{\mathrm{Sm}}$ should be kept as large as possible to ensure the relative error in the difference $s_{\mathrm{Sm}}^2-s_{\mathrm{Lg}}^2$ is small. In Chapter 3, it was shown that a ratio of two is much too small. A ratio of 10 is about the minimum acceptable.

The term $w_{\mathrm{Lg}}w_{\mathrm{Sm}}/(w_{\mathrm{Lg}}-w_{\mathrm{Sm}})$ should also be held to as small a value as possible to minimize the error in the product $[w_{\mathrm{Lg}}w_{\mathrm{Sm}}/(w_{\mathrm{Lg}}-w_{\mathrm{Sm}})](s_{\mathrm{Sm}}^2-s_{\mathrm{Lg}}^2)$. This is accomplished by keeping w_{Sm} small. The limit for w_{Sm} is determined either by the minimum size of test portion required for analysis or by limitations in the sampling equipment and operation.

w_{Lg} and w_{Sm} should also be chosen to encompass the increment weight that most likely will be selected during subsequent sampling, especially if that increment weight is defined by practical considerations of equipment, etc., rather than statistical considerations. The reason for this will become clear in Chapter 5.

Next consider increments. Analysis of equal numbers of increments in each set does not guarantee the most precise estimate of *A* and *B*. The change in the number of increments that will hold s_s^2 to a selected value as a function of s_{Sm} or s_{Lg} is given by

$$\frac{dn}{ds_{Sm}} = 2s_{Sm}\left(\frac{w_{Lg}w_{Sm}}{s_s^2\ w(w_{Lg} - w_{Sm})} - \frac{w_{Sm}}{s_s^2(w_{Lg} - w_{Sm})}\right) \qquad [22]$$

and

$$\frac{dn}{ds_{Lg}} = 2s_{Lg}\left(\frac{1}{s_s^2} + \frac{w_{Sm}}{s_s^2(w_{Lg} - w_{Sm})} - \frac{w_{Lg}w_{Sm}}{s_s^2\ w(w_{Lg} - w_{Sm})}\right) \qquad [23]$$

These equations are first derivatives of the equation

$$n = \frac{A}{ws_s^2} + \frac{B}{s_s^2} \qquad [24]$$

with *A* and *B* defined by Equations 6 and 7.

Comparison of the values for dn/ds_{Sm} and dn/ds_{Lg} will indicate whether the number of increments in the prescribed protocol is more sensitive to errors in s_{Sm} or s_{Lg} in the original sampling experiments. Emphasis can then be placed on obtaining a more precise value by analyzing more increments for the set that controls n to the greater degree. For example, in the sampling of a high-grade Athabasca oil sand for determination of bitumen content, substitution of the values w_{Lg} = 951.95 g, w_{Sm} = 50.62 g, s_{Sm} = 1.86, w = 163 g (i.e., w_{opt}), and s_{s} = 0.14 (1% relative) into Equation 18 and 19 yields $\mathrm{d}n/\mathrm{d}s_{\mathrm{Sm}} = 50$ and $\mathrm{d}n/\mathrm{d}s_{\mathrm{Lg}} = 70$. An error of 0.1 in the estimate of s_{Sm} or s_{Lg} would cause errors of 5 and 7 in the estimate of the number of increments n that would hold s_{s} to 1% relative. Either error is relatively small, considering that the calculated value of n for increments weighing w_{opt} falls in the range of 80.

The values $\mathrm{d}n/\mathrm{d}s_{\mathrm{Sm}}$ and $\mathrm{d}n/\mathrm{d}s_{\mathrm{Lg}}$ need not be similar. If, for example, s_{Lg} was 1.25 in the case described above, w_{opt} would have been 70 g and values of 134 and 37 for $\mathrm{d}n/\mathrm{d}s_{\mathrm{Sm}}$ and $\mathrm{d}n/\mathrm{d}s_{\mathrm{Lg}}$ would have been found. More effort would have been required to obtain a precise estimate of σ_{Sm} than of σ_{Lg}.

However, χ^2-statistics indicate that to achieve a 0.1% uncertainty in the estimate of σ_{Sm} and σ_{Lg} at the 68% level of confidence, approximately 50 to 80 increments of each size would need to be collected and analyzed. This level of preliminary sampling and analytical effort to estimate A and B is sometimes the rationale invoked to completely avoid the characterization of sample variability. Fortunately a sizeable reduction in analytical effort can be achieved through compositing of increments prior to analysis.

4.2.2 Use of Composites to Estimate A and B

Visman's equation can be modified to incorporate data from the analysis of composites as follows:

In Equation 6 the variances associated with collection of one (n = 1) small and one large increment are

$$s_{Sm}^2 = \frac{A}{w_{sm}} + B \text{ and } s_{Lg}^2 = \frac{A}{w_{Lg}} + B \qquad [6]$$

Rearranging

$$B = s_{Sm} - \frac{A}{w_{Sm}} \text{ and } B = s_{Lg}^2 - \frac{A}{w_{Lg}} \qquad [25]$$

Simultaneous solution for A yields

$$A = \frac{w_{Lg} w_{Sm}}{w_{Lg} - w_{Sm}} (s_{Sm}^2 - s_{Lg}^2) \qquad [26]$$

Analyses conducted on composites of i_{Sm} small increments of weight w_1 or i_{Lg} large increments of weight w_2, selected so that $i_{Sm} w_1 = w_{Sm}$ and

$i_{Lg}w_2 = w_{Lg}$, give variances of

$$s_{Sm}^2 = \frac{A}{i_{Sm}w_1} + \frac{B}{i_{Sm}} \text{ and } s_{Lg}^2 = \frac{A}{i_{Lg}w_2} + \frac{B}{i_{Lg}} \qquad [27]$$

From these relations one obtains

$$B = i_{Sm}s_{Sm}^2 - \frac{A}{w_1} = i_{Lg}s_{Lg}^2 - \frac{A}{w_2} \qquad [28]$$

and

$$A = \frac{w_2w_1}{w_2 - w_1}\,(i_{Sm}s_{Sm}^2 - i_{Lg}s_{Lg}^2) \qquad [29]$$

It is crucial that the increments comprising each composite are themselves randomly selected. If the increments forming each composite were those selected consecutively in time on a moving belt or from a single zone of the bulk sample, an overestimate of segregation would result.

The analysis of 20 to 30 composites is the minimum recommended for estimating A and B, but by compositing, analytical effort is expended efficiently. An example of a calculation using composites is given in Table 21 in which data from the analysis of high-grade oil sands are used. Here w_2 = 952 g, w_1 = 50 g, i_{Lg} = 2 representing a compositing or averaging of two data points from the large increments and i_{Sm} = 1 indicating no compositing of the small increments. The estimates of A and B agree well with the estimates using the original non-composited data.

Table 21: The use of composites prepared from randomly selected 950-g increments to calculate Visman's constants

Increment Location	Bitumen %	Solids %	Water %
1-3-24, 1-1-23	14.34	84.27	0.94
1-3-9, 1-1-22	14.70	83.99	0.88
1-1-10, 1-1-30	14.21	84.28	1.15
1-1-12, 1-4-27	13.52	84.41	1.72
1-5-38, 1-5-21	14.00	83.95	1.13
1-3-18, 1-1-9	13.73	84.59	1.16
1-3-7, 1-3-1	15.30	83.53	0.89
1-2-14, 1-4-13	15.52	83.54	0.69
1-5-19, 1-1-20	14.87	84.00	0.81
1-3-21, 1-4-34	14.13	84.21	1.27
1-3-27, 1-1-18	13.76	84.04	2.13
1-4-3, 1-1-4	13.56	84.29	1.73
1-3-17, 1-4-21	15.64	83.10	1.73
1-1-33, 1-3-31	14.33	83.77	0.89
1-1-1, 1-1-32	14.49	83.46	1.39
1-3-8, 1-2-12	15.86	83.14	1.67
1-3-26, 1-2-29	13.05	84.49	0.64
1-1-37, 1-4-26	13.34	83.78	2.11
1-2-27, 1-5-24	14.12	83.82	2.51
1-5-23, 1-1-27	13.75	83.70	1.56
1-4-32, 1-5-10	15.01	83.34	2.23
1-1-17, 1-4-12	13.86	83.99	1.19
1-3-11, 1-3-2	14.46	83.52	1.03
1-2-18, 1-3-5	14.03	83.72	1.82
s_o	0.745	0.411	0.521
s_a	0.269	0.269	0.141
s_{Lg}	0.70	0.31	0.50
$A = \frac{w_{Lg} w_{Sm}}{w_{Lg} w_{Sm}} ({s_{Sm}}^2 - 2{s_{Lg}}^2)$ (a)	133	19.0	84.1
A (original value)	134	16.4	86.1
B $2{s_{Lg}}^2 - A/w_{Lg}$	0.83	0.17	0.41
B (original value)	0.82	0.22	0.37

(a) A value of s_{Sm} of 1.86 taken from the analysis of 48 50-g increments was used.

4.2.3 Increment Pair Approach

In the increment-pair approach, the intraclass correlation coefficient and particle size provide the basis for estimating A and B. Uncertainties in the assumptions about particle size have been identified in the case of a non-particulate material such as oil sand, but even in the case of hard minerals, average particle size is not always easily defined. For polydisperse solids, because the larger particles tend to influence sampling uncertainty most, the value for average particle mass should be based upon the size of screen upon which 5% of the material is retained, as recommended by Gy (6).

However, the issue becomes somewhat more complicated because the physical dimensions of the particles may not represent a particle from a sampling viewpoint. In particular, sampling variance as defined by Gy (6):

$$s^2 = fgclu^3/w \qquad [2]$$

is a function of the liberation factor, l, the ratio of the pure particles of the component of interest to the diameter of the coarsest 5% of the particles in the sample, as well as the dimensions, u, of the coarsest particles. Therefore, in the sampling of coal for determination of ash content, is Visman's value of m derived from the lump size of the coal the most suitable one, or should it incorporate some term including the dimensions of the ash-forming constituents of coal? Appropriate experiments to resolve this question for coal including both the two-increment size and increment-pair approaches have not been reported.

Due to the nature of the calculation of r, the mathematical value assigned to it tends to be imprecise. The three estimates of ρ, the true intraclass correlation coefficient, calculated for one component in Athabasca oil sand sometimes had a range that exceeded the mean value by a factor of two. Each estimate of ρ was based on analysis of approximately 12 pairs of increments - a number which would be inadequate as a basis for forming sampling protocols for most systems.

A difficulty that arises in obtaining an accurate estimate of ρ lies in the appropriate selection of increments. Both the location of each pair and the relative orientation of the members within each pair of increments must be randomly selected. Figure 7a,b illustrates orientations that could lead to significant errors in r. In Figure 7a the pairs tend to be oriented along strata; this leads to low estimates of σ_w and high estimates of σ_b. Then, r provides a high estimate of ρ and oversampling would be prescribed for a specified level of s_s. Figure 7b illustrates orientation at right angles to prevailing stratification; this leads to low estimates of ρ and so to undersampling.

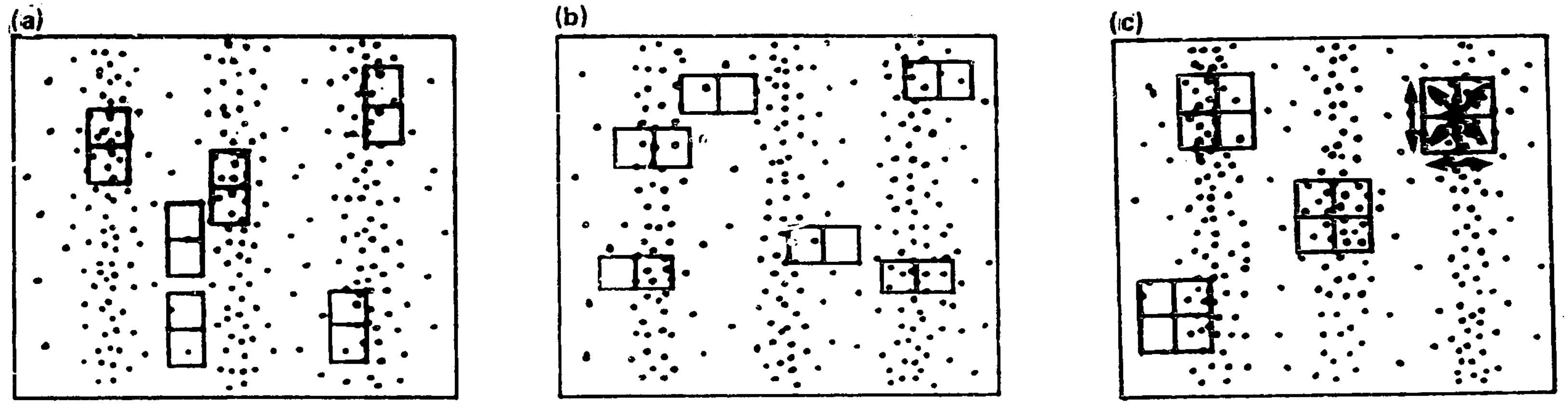

Figure 7. Orientations of pairs of increments in a segregated population that lead to overestimation (a) and underestimation (b) of the degree of segregation. Arrows in section (c) indicate direction which pairs of increments may be evaluated to assess effects of orientation.

"Directional" segregation or banding in a population can be identified by collecting increments in sets of four rather than in pairs (Figure 7c). Values of r for four orientations can be calculated and compared. They will be approximately equal if segregation occurs in patches but will differ if banding is present. Banding in a sample having a significant third dimension can be identified by collection of an additional pair of increments in the z axis.

Orientation of increment pairs is not a problem when sampling from a flowing stream or moving belt, provided the sampling device selects increments incorporating a complete cross section of the stream. Collection of only a fraction of the stream cross section at any one time is not recommended because lateral or vertical segregation may bias the results.

4.3 Design of Sampling Protocols for Application to Unknown Populations

4.3.1 Tests for Segregation

Application of Ingamells' constant to a bulk material is valid only when the particles in the sample are well-mixed; under these conditions sampling uncertainty associated with collection of a single increment of weight w will be the same as the uncertainty associated with collecting x_f increments of weight w/x_f. It is possible to determine with high confidence whether a material is well-mixed by analyzing two sets of increments of widely differing weights, w_{Lg} and w_{Sm}, for under well-mixed conditions

$$s_{Lg}^2 w_{Lg} = s_{Sm}^2 w_{Sm} \qquad [30]$$

Here s_{Lg} and s_{Sm} are estimates of σ_{Lg} and σ_{Sm}, the true population standard deviations, and are themselves relatively imprecise unless large numbers of increments are analyzed. A one-tailed *F*-test (44) should be used to determine whether σ_{Lg} and $(w_{Sm}/w_{Lg})^{1/2}\sigma_{Sm}$ differ significantly at a specified confidence level. The consequences may be severe if one decides a sample is well-mixed when it is not; therefore the test should be applied at a 90% or lower level of confidence. If the null hypothesis is rejected, $\sigma_{Lg} > (w_{Sm}/w_{Lg})^{1/2}\sigma_{Sm}$, the sample is considered to be segregated.

In a second test for segregation, the intraclass correlation coefficient, r, is tested in comparison with statistical tables to determine whether it is likely that $\rho = 0$. If that hypothesis is rejected, the population is considered to be segregated.

A third test involves analysis of several sets of increments over a range of weights varying by at least a factor of 10. Approximately 30 data points for each increment weight must be collected to hold the error in s (and therefore R) to 25% relative at the 95% level of confidence (45).

Rearrangement of Equation 5 to $R^2 = K_s(1/w)$ suggests that for well-mixed materials a plot of R^2 against $1/w$ on a linear scale will yield a straight line of slope K_s and an intercept of zero. As a result it is tempting to decide the population is well-mixed if the standard deviation in the slope is small. However, the y-intercept of the line is the measure of segregation. If the confidence limits around the y-intercept do not encompass the origin in a plot of R^2 vs. $1/w$, the population may be considered to be segregated. Such a plot provides much clearer proof of segregation than a subjective evaluation of the curvature of the lines in Visman's original plots of $\log(s_s{}^2)$ vs. $\log(w)$ (11).

4.3.2 Relationships Between Sampling Constants

A value for K_s calculated from Equation 5 for a segregated population has a different meaning than K_s for a well-mixed population. In the latter K_s represents the weight of a single increment that will hold R to 1% at the 68% level of confidence; in the former wR^2 represents the weight of a composite made up of increments of the weight used to calculate the sampling constant that will hold R to 1% at the 68% level of confidence. When sets of increments from a segregated sample are collected, the numerical value of wR^2 from Equation 5 increases with increasing w. Values for wR^2 increase by a factor of approximately 5 upon increasing, from 50 g to 500 g, the weight of increments of Athabasca oil sand collected for determination of bitumen, water, and solids content (Table 14).

In view of these results the relationship between Ingamells' constant K_s and Visman's constant A, given by

$$A = 10^{-4}K_s\bar{x}^2 \qquad [31]$$

in Reference 20, is valid only for well-mixed materials where Visman's B term equals zero. When B equals zero

$$s_s^{\,2} = A/wn \qquad [32]$$

and

$$K_s = wR^2 = \frac{10^4 ws_s^{\,2}}{\bar{x}^2} = \frac{10^4 wA}{\bar{x}^2 wn} = \frac{10^4 A}{\bar{x}^2 n} \qquad [33]$$

When n equals 1, K_s=$10^4A/\bar{x}^2$, which rearranges to Equation 31. Thus, when B does not equal zero, Equation 31 does not apply. In a similar manner, the relation between Visman's constant A and the Gy sampling constants

$$A = fgclu^3 \qquad [34]$$

is appropriate only when segregation is absent. It should be noted that Gy in his overall work on sampling of particulate materials on an industrial scale does address long-term variability through the use of semi-variograms but that variability is not defined in terms of a sampling constant.

4.3.3. Effect of Number of Increments on Sampling Uncertainty

In a sampling operation whose cost is controlled by the total amount of sample rather than the number of increments collected, reduction in sampling uncertainty can be achieved while minimizing the increase in expense by collecting more but smaller increments. Increasing the number of increments, n, without changing the total weight collected, wn, will not alter the variance for well-mixed populations but will reduce it for segregated populations. Figure 8a,c illustrates the effect of increasing n while decreasing w for a well-mixed sample. For n increments

$$s_s^2 = A/wn \qquad [32]$$

and for $x_f n$ increments, each weighing w/x_f

$$s_s^2 = \frac{A}{(w/x_f)\,(x_f n)} = \frac{A}{wn}$$

Increasing the number of increments from a segregated population without altering the total weight of sample collected reduces the sampling variance when $x_f > 1$ because

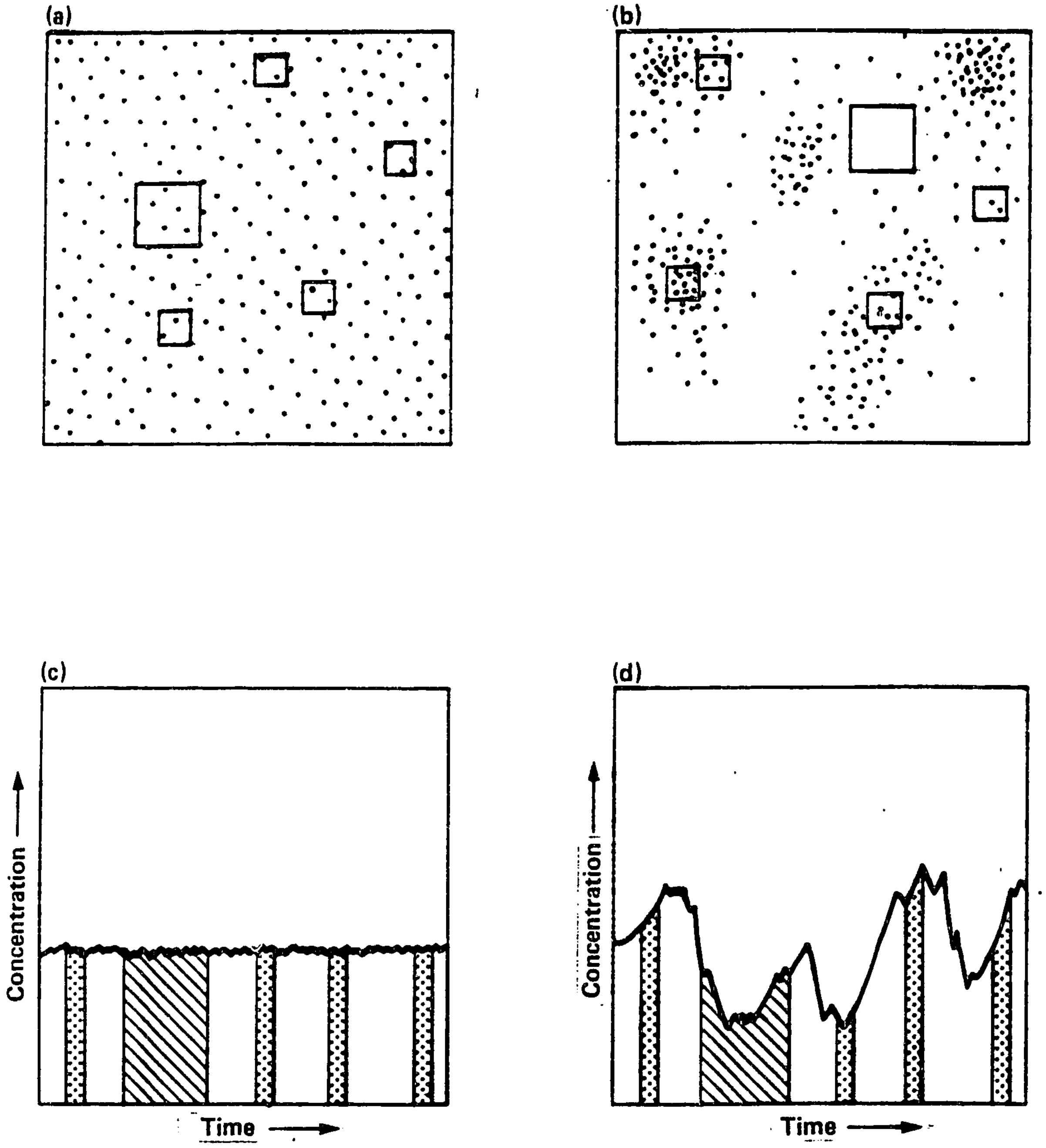

Figure 8. Representation of effect on sampling uncertainty of increasing increment size and number collected from well-mixed (a, c) and segregated (b, d) populations. (a) and (b) represent sample increments of different size on a two-dimensional surface; (c) and (d) represent sampling on a belt or transect.

$$\frac{A}{(w/x_f)(x_f n)} + \frac{B}{x_f n} = \frac{A}{wn} + \frac{B}{x_f n} < \frac{A}{wn} + \frac{B}{n}$$

This situation is depicted in Figure 8b,d. As the number of increments is increased for a segregated population, more strata are sampled and the composite is more representative of the population than a single increment of the same total weight. But when $x_f < 1$ (indicating a decrease in the number of increments for a fixed total weight), then

$$\frac{A}{wn} + \frac{B}{x_f n} > \frac{A}{wn} + \frac{B}{n}$$

and some sampling precision is lost.

4.3.4 Effect of Weight of Increments on Sampling Uncertainty

For segregated populations the effect on s_s^2 of a change in increment weight cannot be determined unless estimates of A and B are known. Changes in w do not reduce the contribution of the segregation term B to the sampling variance. From Equation 6, when w is changed by a factor x_f, the sampling variance changes from

$$\frac{A}{wn} + \frac{B}{n} \quad \text{to} \quad \frac{A}{wx_f n} + \frac{B}{n},$$

not to

$$\left(\frac{A}{wn} + \frac{B}{n}\right)\frac{1}{x_f}$$

This point is illustrated in Figure 8a,b, which represents distributions of a component in a well-mixed and a segregated population. Increasing the size of increments collected from a well-mixed population reduces the uncertainty due to random distribution. Increasing the size of increments from a segregated population may result simply in the collection of larger segments of a small number of strata; under these conditions s_s is affected only slightly, if at all. The same trend is depicted in Figure 8c,d, which represents concentration as a function of time as a bulk material is transported by conveyor past a fixed detector, or concentration as a function of distance as a detector transects a surface or is lowered in a hole.

The fraction of overall sampling error arising from the segregation variance term in Visman's equation is independent of the absolute values of A and B for a given sampling protocol. For example, when increment weights equal to A/B, defined as the optimum increment weight, w_{opt}, are collected from either a particulate or non-particulate material, 50% of the sampling variance will arise from segregation regardless of the absolute values of A and B. The percentage of overall sampling variance due to segregation as a function of w_{opt} times a factor, x_f, is plotted in Figure 9. The relative reduction in sampling variance in changing increment size, if w_{opt} is known, can be determined from the figure.

Consider the case where increments weighing w_{opt} are collected from a bulk sample. The contribution of A to the total variance is 50% (say 50 units). For $w = 0.25w_{opt}$, A contributes 50/0.25 = 200 units and for

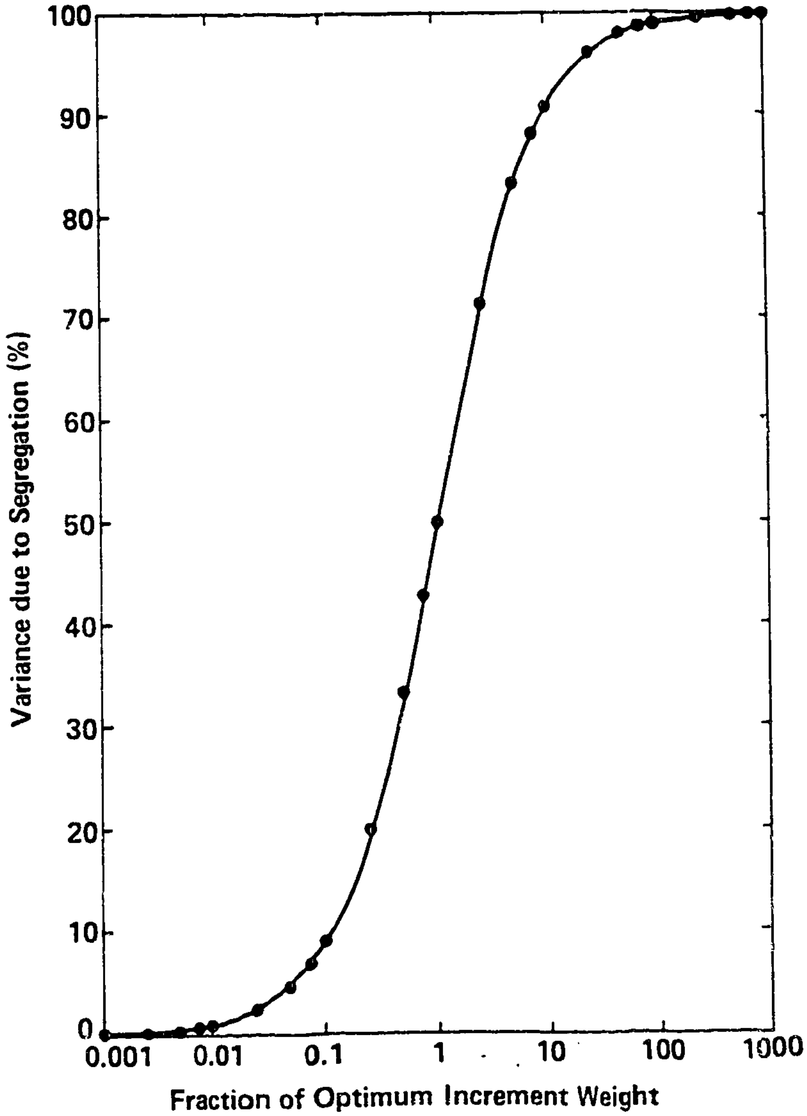

Figure 9. Percentage of error due to segregation as a function of increment weight. The relation is described by log y = 0.0010 (log x)^3 - 0.1335 (log x)^2 + 0.4972 log x + 1.6035. The correlation coefficient is 0.9978.

$w = 5w_{opt}$, A contributes 50/5 = 10 units. Because the segregation variance contributes 50 units whether $w = 0.25w_{opt}$ or $5w_{opt}$, the reduction in total sampling variance by increasing increment weights from $0.25w_{opt}$ to $5w_{opt}$ is (200 + 50) - (10 + 50)/250 = 0.76 or 76%. This observation is tested in Table 22, which lists the sampling variances for the determination of oil, water, and solids on 950-g and 50-g increments of Athabasca oil sand. These weights correspond to approximately $5w_{opt}$ and $0.25w_{opt}$ for these components in this material. The ratio $s_{s,950}^2/s_{s,50}^2$ falls in the range 0.22-0.51, indicating that Figure 9 and the associated calculations reliably estimate reduction in sampling variance, within the limits of the uncertainties in the estimates of sampling variance and w_{opt}.

It can be concluded that, in general terms, changing w has a significant effect when w falls below $10w_{opt}$. In the range 0.1 to $10w_{opt}$, the variances due to random distribution and segregation are of the same order of magnitude so that a reduction in overall variance as a result of decreasing the segregation variance as shown in Figure 9 will occur. Below $0.1w_{opt}$, the decrease in variance due to segregation is not readily apparent from Figure 9 but since the random distribution is the major contributor to overall variance, increasing w still has a

Table 22: Sampling variances for single increments collected from Athabasca oil sand weighing 950 g (~$5w_{opt}$) and 50 g (~$0.25w_{opt}$)

	$s_{s,950}^2$	$s_{s,50}^2$	$s_{s,950}^2/s_{s,50}^2$
High-grade oil sand			
Bitumen	0.96	3.45	0.28
Solids	0.24	0.55	0.44
Water	0.46	2.07	0.22
Low-grade oil sand			
Bitumen	0.49	1.74	0.28
Solids	1.00	1.96	0.51
Water	2.02	4.00	0.51

major effect on overall variance. Only at levels above $10w_{\mathrm{opt}}$ does a change of increment weight have little effect on s_o.

An alternate method for determining the effect of changing increment size on sampling variance is limited to particulate materials. The equation

$$\frac{\sigma_{\mathrm{Lg}}^2}{\sigma_{\mathrm{Sm}}^2} = \frac{w_{\mathrm{Sm}}mz^2}{1 + w_{\mathrm{Sm}}mz^2} + \frac{w_{\mathrm{Sm}}}{w_{\mathrm{Lg}}}\left[\frac{1}{1 + w_{\mathrm{Sm}}mz^2}\right] \qquad [34]$$

describes the relation between $\sigma_{\mathrm{Lg}}^2/\sigma_{\mathrm{Sm}}^2$ and $w_{\mathrm{Sm}}/w_{\mathrm{Lg}}$ for particulate materials over a range of particle size and degree of segregation. Equation 34 is derived from the relation

$$z^2 = B/Am \qquad [9]$$

by

$$mz^2 = \frac{B}{A} = \frac{\sigma_{\mathrm{Lg}}^2 - \frac{A}{w_{\mathrm{Lg}}}}{A}$$

$$= \frac{\sigma_{\mathrm{Lg}}^2}{A} - \frac{1}{w_{\mathrm{Lg}}}$$

$$= \frac{\sigma_{\mathrm{Lg}}^2/\sigma_{\mathrm{Sm}}^2}{A/\sigma_{\mathrm{Sm}}^2} - \frac{1}{w_{\mathrm{Lg}}}$$

$$= \frac{\sigma_{Lg}^2/\sigma_{Sm}^2}{\left[\dfrac{w_{Lg}w_{Sm}}{w_{Lg} - w_{Sm}}\right]\left[\dfrac{\sigma_{Sm}^2 - \sigma_{Lg}^2}{\sigma_{Sm}^2}\right]} - \frac{1}{w_{Lg}}$$

$$= \frac{\sigma_{Lg}^2/\sigma_{Sm}^2}{\left[\dfrac{w_{Lg}w_{Sm}}{w_{Lg} - w_{Sm}}\right]\left[1 - \dfrac{\sigma_{Lg}^2}{\sigma_{Sm}^2}\right]} - \frac{1}{w_{Lg}}$$

$$mz^2 - \frac{mz^2\sigma_{Lg}^2}{\sigma_{Sm}^2} = \frac{\sigma_{Lg}^2/\sigma_{Sm}^2}{\left[\dfrac{w_{Lg}w_{Sm}}{w_{Lg} - w_{Sm}}\right]} - \frac{1}{w_{Lg}} + \frac{\sigma_{Lg}^2}{\sigma_{Sm}^2 w_{Lg}}$$

$$\frac{\sigma_{Lg}^2}{\sigma_{Sm}^2}\left[\frac{1}{\dfrac{w_{Lg}w_{Sm}}{w_{Lg} - w_{Sm}}} + \frac{1}{w_{Lg}} + mz^2\right] = mz^2 + \frac{1}{w_{Lg}}$$

$$\frac{\sigma_{Lg}^2}{\sigma_{Sm}^2} = \frac{\left(mz^2 + \dfrac{1}{w_{Lg}}\right)}{\left[\dfrac{1}{w_{Lg}w_{Sm}/w_{Lg} - w_{Sm}} + \dfrac{1}{w_{Lg}} + mz^2\right]}$$

$$= \frac{\left[\dfrac{mz^2 w_{Lg} + 1}{w_{Lg}}\right]}{\left[\dfrac{w_{Lg} - w_{Sm}}{w_{Lg}w_{Sm}} + \dfrac{1}{w_{Lg}} + mz^2\right]}$$

$$= \frac{\left[\dfrac{mz^2 w_{Lg} + 1}{w_{Lg}}\right]}{\left[\dfrac{w_{Lg} - w_{Sm} + w_{Sm} + mz^2 w_{Lg}w_{Sm}}{w_{Lg}w_{Sm}}\right]}$$

$$= \frac{w_{\mathrm{Sm}}(mz^2 w_{\mathrm{Lg}} + 1)}{w_{\mathrm{Lg}}(1 + mz^2 w_{\mathrm{Sm}})}$$

$$= \frac{w_{\mathrm{Sm}} mz^2}{1 + w_{\mathrm{Sm}} mz^2} + \frac{w_{\mathrm{Sm}}}{w_{\mathrm{Lg}}} \left[\frac{1}{1 + w_{\mathrm{Sm}} mz^2} \right] \qquad [34]$$

Equation 34 was used to generate the bottom three lines in Figure 10. These plots illustrate the relationships between $\sigma_{\mathrm{Lg}}^2/\sigma_{\mathrm{Sm}}^2$ and $w_{\mathrm{Sm}}/w_{\mathrm{Lg}}$ for populations with degrees of segregation of 0, 0.5, or 0.8 and from which small increments containing one particle are collected. The third line from the bottom of Figure 10 suggests that if increments containing one particle ($w_{\mathrm{Sm}}m = 1$) had historically been collected from a population with a degree of segregation of 0.8, an increase in increment size to two particles ($w_{\mathrm{Sm}}/w_{\mathrm{Lg}} = 0.5$) would reduce the sampling variance to 69% of its original value. Figure 10 and Equation 34, therefore, support the concept originally presented in Figure 8 that an increase in increment weight by a factor x causes a reduction in sampling variance by some factor less than x if a population is segregated. The extent of reduction depends on the number of particles in the small and large increments as well as the degree of segregation. The top three lines in Figure 10 were generated from Equation 34 and describe the reduction in sampling variance resulting from increasing increment size when the original increment contains 1, 10, or 100 particles and the population has a degree of segregation of 0.8. A large reduction in sampling variance occurs only if the original increment contains few particles. The relationship between $\sigma_{\mathrm{Lg}}^2/\sigma_{\mathrm{Sm}}^2$

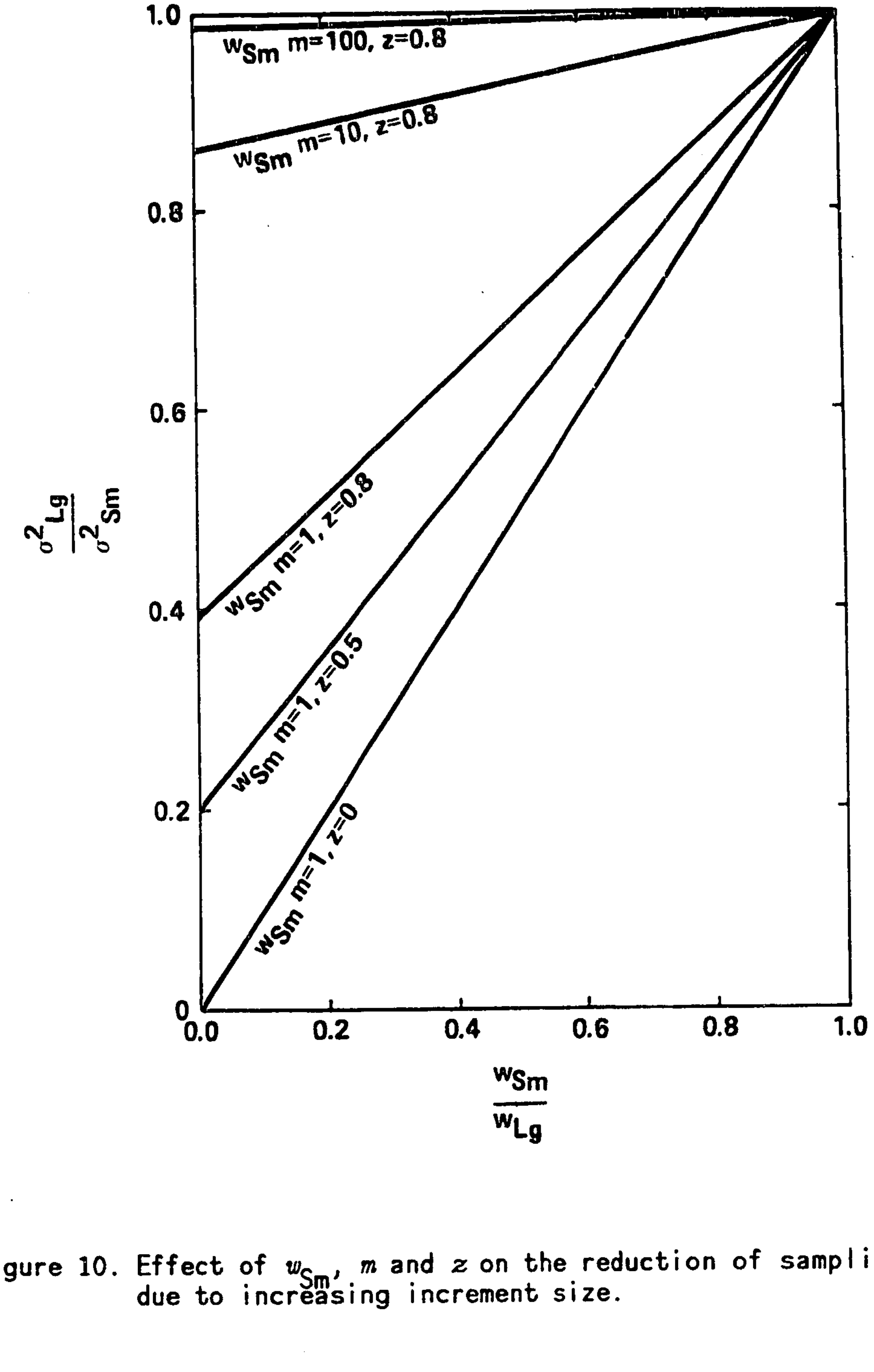

Figure 10. Effect of w_{Sm}, m and z on the reduction of sampling variance due to increasing increment size.

and w_{Sm}/w_{Lg} can be established for any combination of w_{Sm}, w_{Lg}, m, and z by substitution of the appropriate values into Equation 34.

If on average, we consider that the oil sands studied in Chapter 3 had an average particle mass of 20 g and a degree of segregation of 0.5, Equation 34 suggests that increasing the increment weights from 50 to 950 g would reduce the variance to 0.4 times s_{50}^2. Although considerable variation in the ratio s_{950}^2/s_{50}^2 exists in the last column of Table 22, the ratios on average fall in the range of 0.4.

Given the predictions in Figure 9 and 10, the statement that a valid sampling protocol for a segregated population can be set up using a single sampling constant, as long as the increment weight chosen to initially evaluate the variability of the population is not altered in subsequent sampling, should be re-considered. Clearly any increment weight above $10w_{opt}$ originally chosen to calculate the single sampling constant, be it an Ingamells'-type constant, or the constant from classical statistics defined by

$$n = \frac{t^2 s_s^2 (10\ )^4}{R^2\ \bar{x}^2} \qquad [17]$$

is also a reasonable estimate of variability at any other increment above $10w_{opt}$. However, the effort expended to define w_{opt} will also yield an estimate of segregation so the question of the value of a single sampling constant then becomes irrelevant.

4.4 Conclusions

1. A single sampling constant such as Ingamells' constant, K_s, for well-mixed materials can be used to describe the variability of a segregated material. The sampling variance associated with the collection of a specified number of increments can be estimated only if the increments are of the same size used to calculate the constant or if variability at increment weights greater than $10w_{opt}$ is being estimated. Sampling uncertainty is little affected by changing the increment weight, w, if w is greater than 10 times the optimum increment weight. Visman's sampling theory, which incorporates a segregation constant, permits estimation of variability at different increment-size levels. The degree of segregation, z, and the confidence limits in the estimate of z for a segregated population can be estimated by plotting $\sigma_{Lg}^2/\sigma_{Sm}^2$ against w_{Sm}/w_{Lg} over a range of increment weights.

2. Visman's two approaches for calculating the sampling constants A and B can be combined to determine a theoretical particle mass for a nonparticulate material. Use of the theoretical particle concept

explains the need to collect larger samples from some populations if they are to be representative. The concept also demonstrates limitations in the use of an intraclass correlation coefficient-average particle mass relation to calculate A and B. Therefore, the two-increment-size approach of Visman, even though not statistically rigorous, is preferred when sampling nonparticulates.

3. Simple mathematical calculations are described in this chapter for the estimation of errors in A and B (Equations 22 and 23) and for the estimation of A and B through the analysis of composites (Equation 29).

5. A CRITICAL EVALUATION OF THE LIMITATIONS OF THE TWO-SAMPLING CONSTANT APPROACH TO DESCRIBING VARIABILITY

5.1 Correlation Between Mathematically-Simulated and Real Populations for Studies of Sampling Theory

Because large quantities of data must be generated to develop and understand sampling theories, a data collection strategy involving collection and analysis of real samples is highly impractical. For this reason, Visman chose to carry out his detailed sampling studies on a sampling board with dimensions of 100 x 100 spaces (11). On this grid of 10,000 spaces he could assign values of '1' as denoted by lead balls or '0' as denoted by empty locations in patterns designed to reflect populations of varying concentrations and degrees of segregation. Sampling was carried out by counting the number of lead balls within an area of specified size and location. The eventual adoption of his sampling theory by the American Society of Testing and Materials (12) for sampling of bulk shipments of coal attests to the successful correlation that can be made between artificial and real populations.

While use of the sampling board simplified sampling studies, mathematical creation of populations and sampling of those populations by computer programming undoubtedly represents the next step in easing the workload. A reference to this method of studying sampling has been provided by Gould and Visman (46) who duplicated exactly Visman's original experiments in a two-dimensional array of 100 x 100. They determined population variability at the 1, 3 x 3 and 9 x 9 increment sizes chosen by Visman on the manual sampling board. Naturally, this set of experiments led to the same conclusions as those carried out on the sampling board.

Gould and Visman's programming can be simplified even further to deal with a one-dimensional array which would represent sampling in time from a continuous stream or from a transect across a population. Studies on this type of array occupy considerably less blocks on the computer than sampling studies of two-dimensional arrays, thereby permitting studies of larger populations and collection of larger increments in relation to particle or patch size.

Central to the Visman theory of sampling is the hypothesis that the degree of segregation observed in a population is independent of increment size. Yet, Visman's equation itself proves that B at some point must change with increment size because when $w = \infty$ at which point $s_s^2 = 0$ (i.e. there is no sampling error), the equation would predict $s_s^2 = B/n$.

In this chapter, the limitations of the Visman equation that fail to predict this occurrence are examined. In particular, the possibility of deviations from the general equation occurring at very small increment sizes is examined.

5.2 Experimental

All of the sampling experiments described in this chapter were carried out on a VAX computer (Digital Corporation, Maynard, Massachusetts) by execution of programs written in Fortran 77. A typical program consisted of two major functions, development of a population of known characteristics in the form of a 100,000 unit one-dimensional array (initially some populations described by continuous mathematical functions were studied), and repeated samplings at specified increment sizes to calculate the sampling variance as a function of increment size. Further calculations and plotting routines were carried out using RS/1 statistical software licensed by Bolt, Beranek and Newman of Cambridge, MA.

5.3 Results and Discussion

5.3.1 Populations Described by Continuous Mathematical Functions

For ease of programming the first populations studied were sine wave functions intended to approximate from a sampling perspective square-wave functions having y-values of 1 or 0. Table 23 lists the program describing sampling from the function $y = 1 + \sin(x)$. In DO LOOP 100, a sampling location is selected by use of a random

Table 23: Program for sampling from the function $y = 1 + \sin(x)$

```
c    Program thes1
c    This program calculates the effect of increment width on
c    sampling uncertainty for the equation y = 1 + sin(x).

      Integer i, j, seed
      Real ytotal, dev, devtotal, w, stdev, average, x(400), y(400)
      Open(unit=3, file='qmsque', status='new')

      Print*, 'Enter a seed number for sampling.'
      Read*, seed

      pi=3.141593
      j=400
      Write(3,1002)
1002  Format(2x, 'This is an output for program thes1.')
      Write(3,1000)seed, j
1000  Format(2x, 'Seed:', 2x, i8, 3x, 'Sample Size:', 2x, i4)
      Do 300 w = 0.785398, 37.699112, 0.785398
      ytotal=0.0
      Do 100 i= 1, j
      x(i)=ran(seed)*999.026464
      y(i)=((x(i)+w)-cos(x(i)+w)-x(i)+cos(x(i)))/w
      ytotal=ytotal+y(i)

100   Continue
      average=ytotal/float(j)


      devtotal=0.0
      Do 200 i = 1, j
      dev=(y(i)-average)**2.0
      devtotal=devtotal+dev

200   Continue
      stdev=sqrt(devtotal/(float(j)-1.0))
      wpi=w/pi
      Write(3,1001)wpi, average, stdev
1001  Format(2x, 'Width:', f10.6, 3x,
     +'Mean:', 2x, f9.6, 3x, 'Std. Dev.:' 2x, f8.6)
300   Continue
      Stop
      End
```

number between 0 and 1 multiplied by 999.026464 (or 318.0000π). By limiting the possible sampling locations to an even multiple of π, rather than say a whole number like 1000, all sections of the sine wave had an equal probability of being selected for sampling.

In the same DO LOOP, the average value of the function over an increment width w was calculated by integrating the area under that section of the curve and dividing by w. For each value of w ranging from 0.785398 (0.25π) to 37.699112 (12π) in steps of 0.25π, a sampling variance based on 400 individual sample increments was calculated (DO LOOP 200).

In contrast to the expected decrease in sampling variance with increasing increment size, the variance-increment size relationship was cyclic in nature as shown in Figure 11. At increment widths of multiples of 2π (i.e. integer multiples of the sine wave period) sampling variance was zero. Maximum sampling variances occurred at increment widths corresponding to integer multiples of half the width of the sine wave period.

Sampling variance-increment size relationship shown in Figures 12 to 14 for the functions

$$1 + \frac{\sin(x)}{2} + \frac{\sin(x/2)}{2},$$

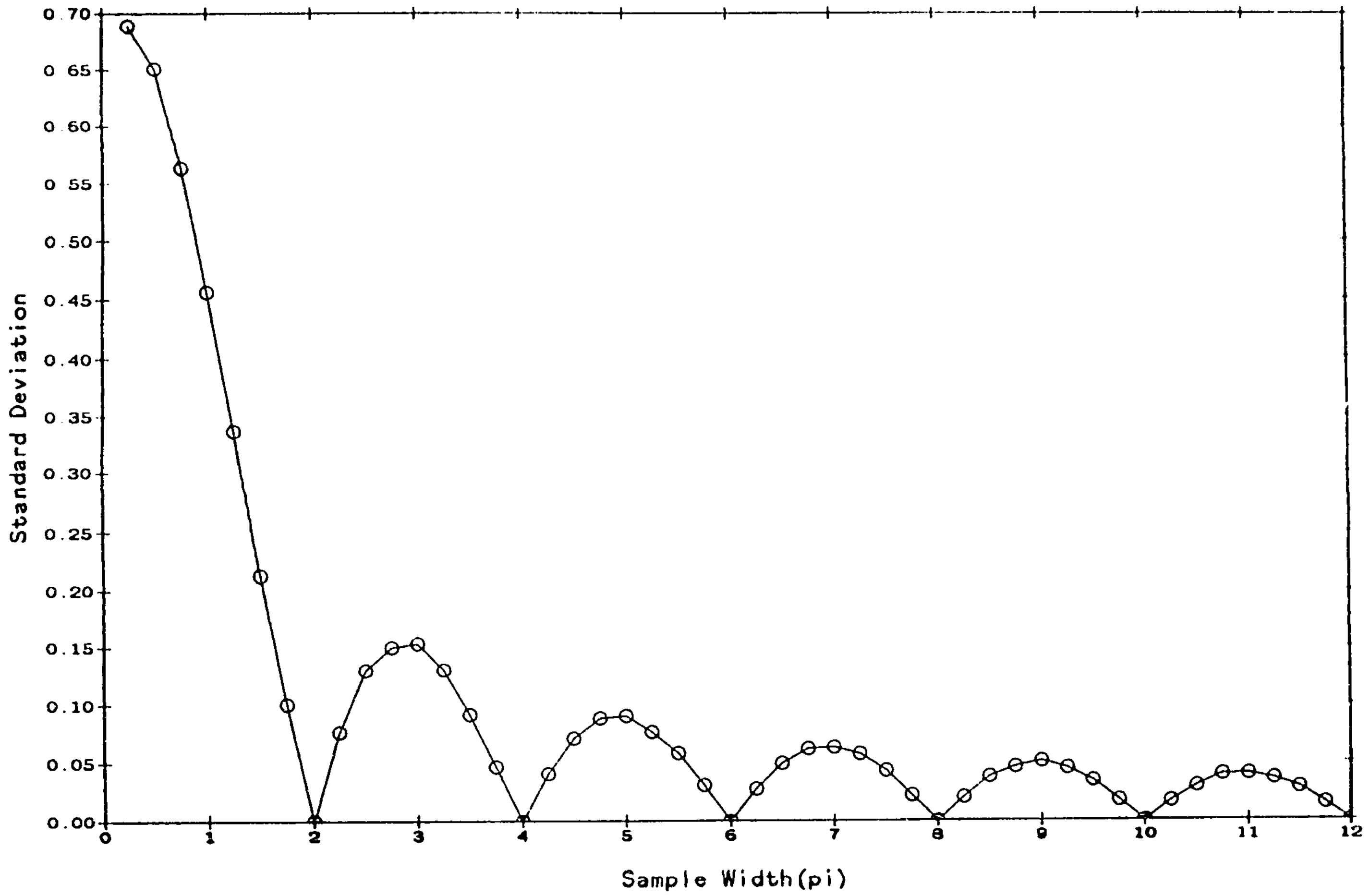

Figure 11. Relationship between increment size and sampling uncertainty for a continuous signal described by $y = 1 + \sin(x)$.

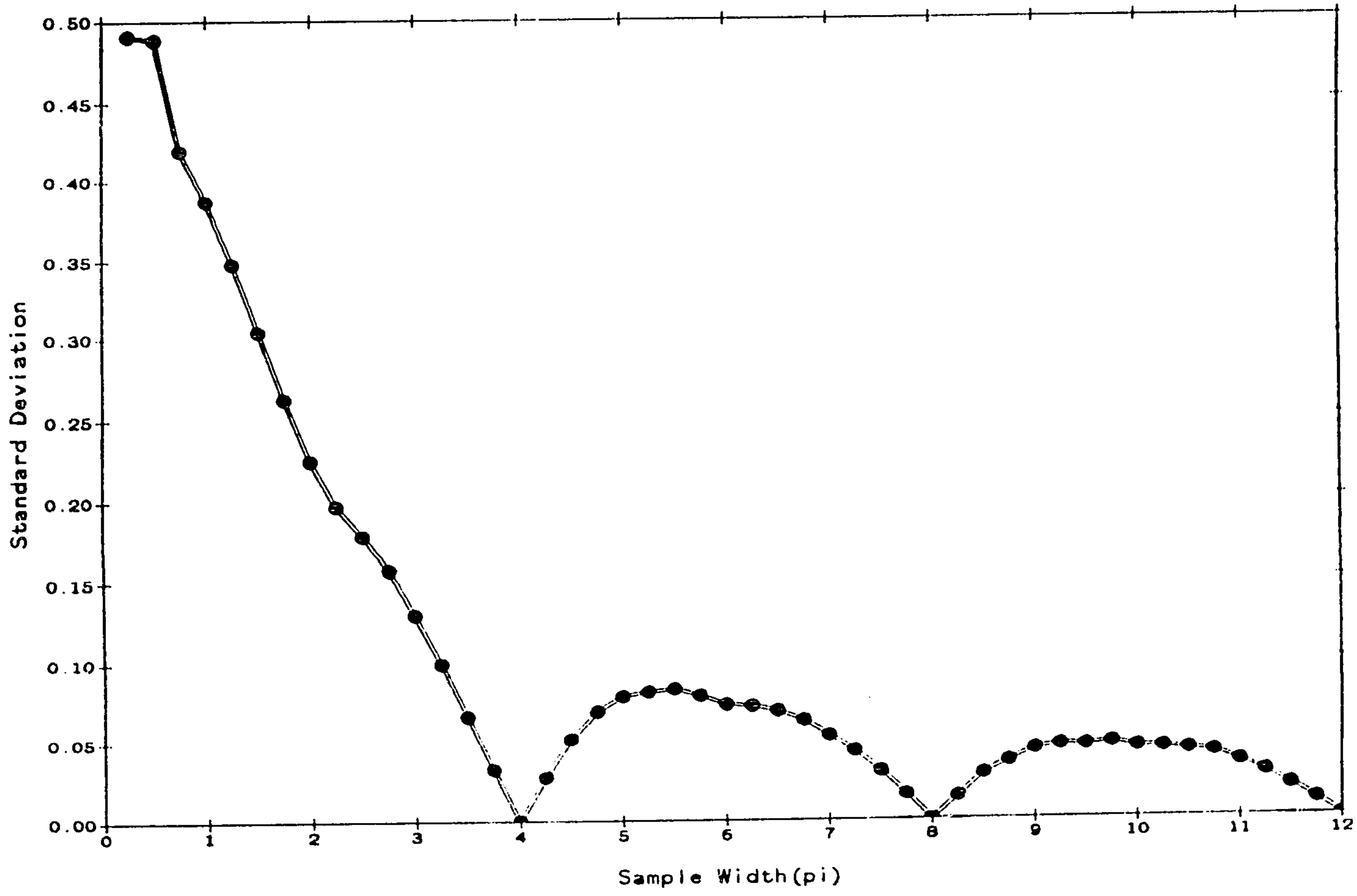

Figure 12. Relationship between increment size and sampling uncertainty for a continuous signal described by $y = 1 + \frac{\sin(x)}{2} + \frac{\sin(x/2)}{2}$

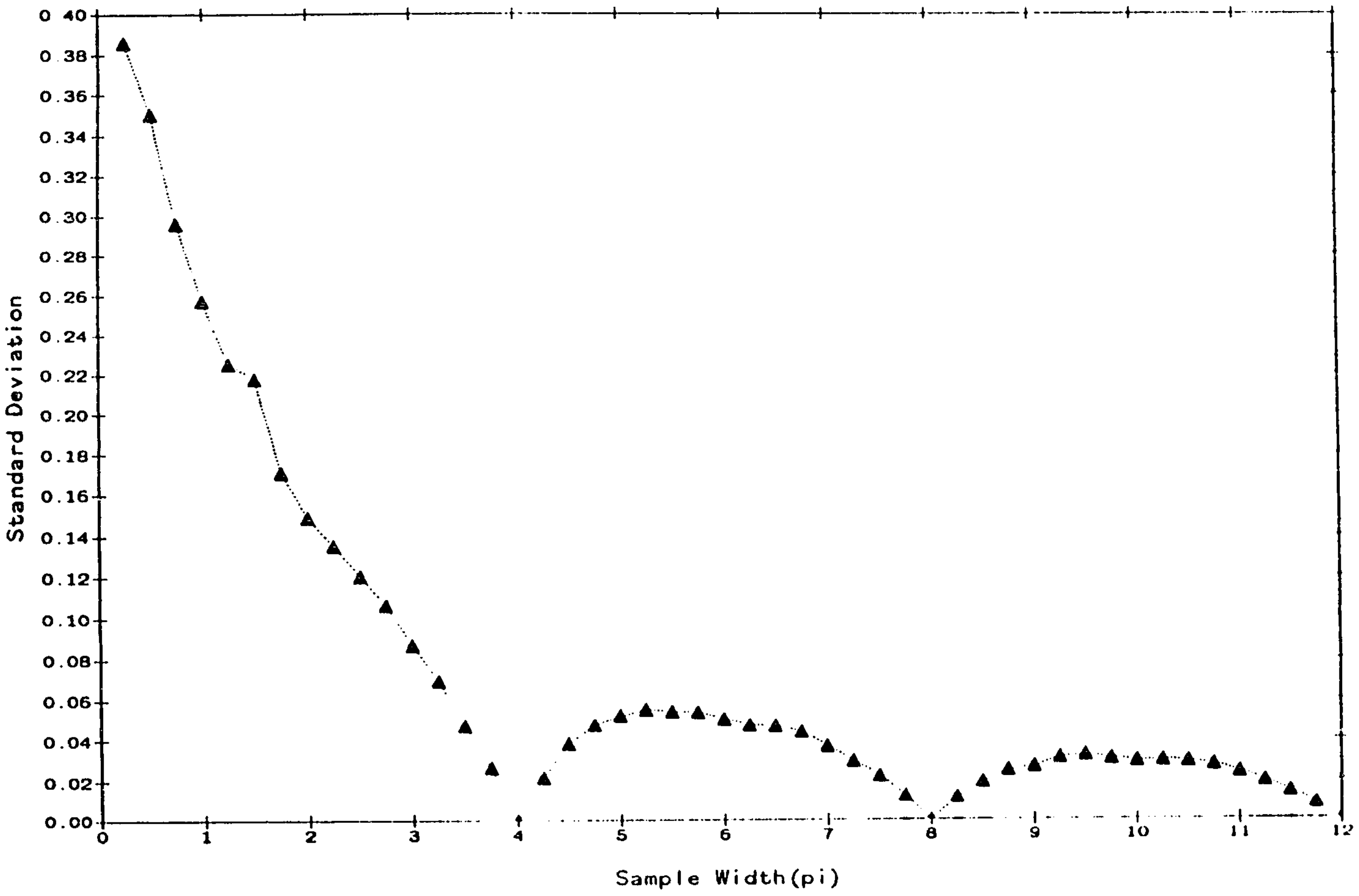

Figure 13. Relationship between increment size and sampling uncertainty for a continuous signal described by $y = 1 + \frac{\sin(x)}{3} + \frac{\sin(x/2)}{3} + \frac{\sin(2x)}{3}$

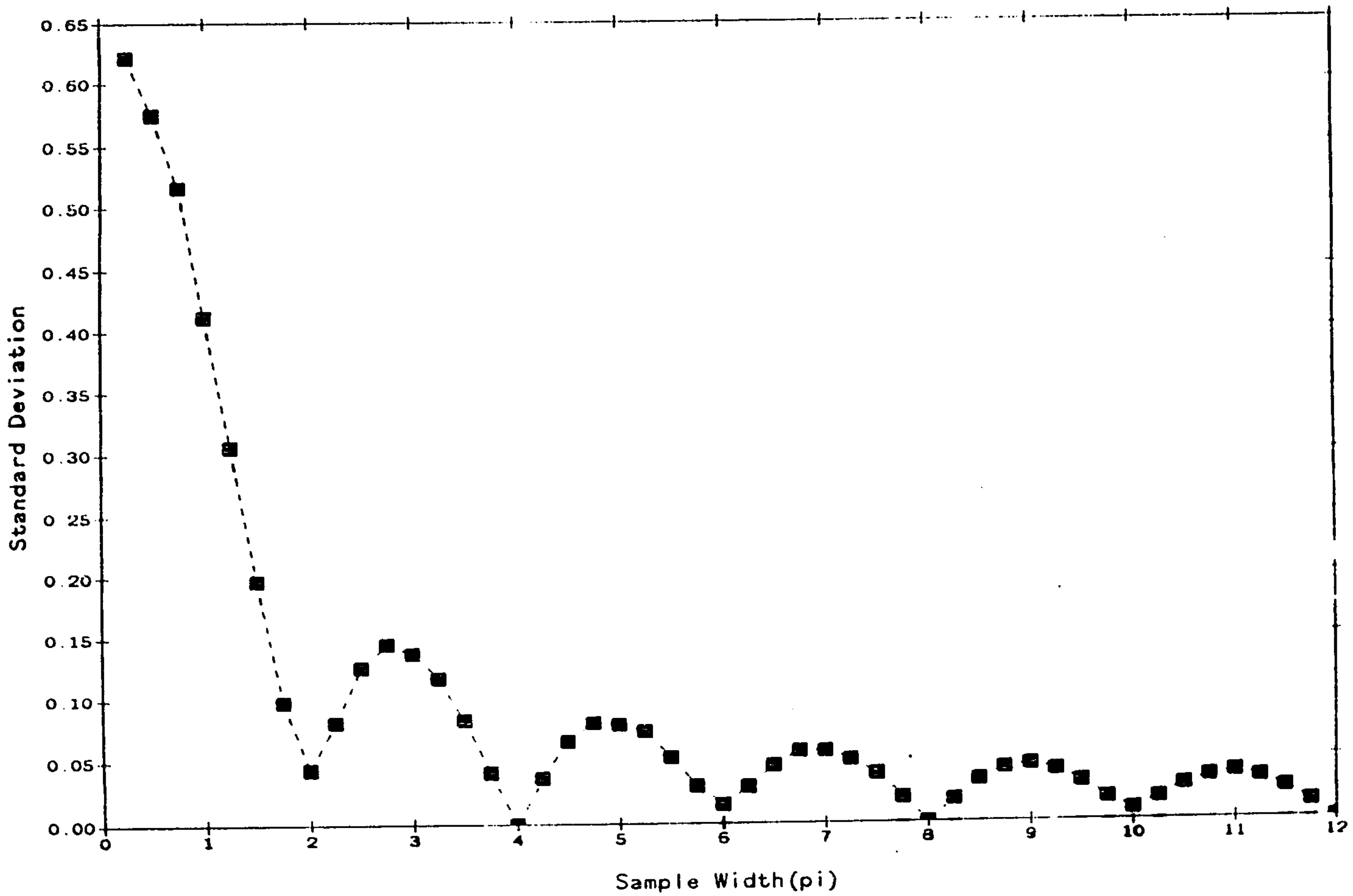

Figure 14. Relationship between increment size and sampling uncertainty for a continuous signal described by $y = 1 + 0.1 \sin(x/2) + 0.9 \sin(x)$.

$$1 + \frac{\sin(x)}{3} + \frac{\sin(x/2)}{3} + \frac{\sin(2x)}{3}\text{, and}$$

$$1 + 0.1 \sin(x/2) + 0.9 (\sin x)$$

showed the same reduction of sampling variance to zero at increment widths corresponding to integer multiples of the period of the total function as well as secondary minima at increment widths corresponding to integer multiples of the periods of the individual terms within the functions. It can be concluded therefore that the Visman general equation for sampling only applies to populations in which the patches or clusters of the component of interest causing segregation are themselves randomly distributed.

While most cyclic populations in nature probably will have relatively large periods, sampling of soil is one situation where calculation of a random and a segregation constant may be suspect. James and Dow (47) have identified three scales of soil variability in a fertilized soil:

Microvariation, the variability between points in the soil that are separated by fractions of an inch, may be controlled by the effects of individual fertilizer pellets on the soil nutrients around it.

Mesovariation, the variability between points in the soil that are separated by a few inches or a few feet, may be affected by the mechanics of application of the fertilizer.

Macrovariation, the soil variability between points separated by a few or many hundreds of feet is a function of the natural variability of the soil.

The computer simulation described here suggests that the mesovariation, which is the most likely to be cyclic and of a fixed period, can be reduced to its minimum value if the sampling tool used to collect the soil is of the same width as the cyclic pattern. However, some mesovariation may remain due to different concentrations of fertilizer in different rows - something which was not calculated in the computer simulation since all cycles had the same amplitude.

To summarize, when the increment width and an integer multiple of the cycle period correspond, no bias errors will occur even when the sampling interval corresponds to the period within the population. Otherwise the superimposition of a systematic sampling plan onto a population of periodic fluctuations can cause serious biases in data.

5.3.2 Populations Described by a One-Dimensional Array

In his discussions of the sampling board experiments with Duncan, Visman had stated that results from the two-dimensional array could be used to determine sampling protocols for one dimension from say, a conveyor belt of coal, provided the sample comprised a complete cross-section of the stream (11). Therefore, it is considered that the findings from this study using a one-dimensional array apply equally to sampling in two or three dimensions.

In this work, an array size of 100,000 was chosen so that even at increment sizes of 1000, the bias introduced into the sampling variance as a result of sampling from a finite population was negligible. Corrections need only be made when the increments collected comprise 10% or more of the population (48). In addition, by using an array of 100,000 elements, segregated populations with patch or cluster sizes much smaller than the increment size could be studied. This had been studied briefly by Visman and Duncan in their discussions on sampling theory (13, 14, 15).

To understand the populations simulated in this study, it is helpful to be able to visualize how a population of a defined degree of segregation can be created in an array. A completely segregated array, 25% occupied by '1' values, has values of '1' assigned to the first 25,000 elements and values of '0' assigned to the last 75,000 elements. For the same number of '1' assignments, a completely unsegregated population has 25,000 '1' values randomly distributed through the population. Degrees of segregation between 1 and 0 can be simulated by converting a randomly-selected portion of the 25,000 '1' values in the segregated population to 0 and then randomly selecting an equal number of elements in the remaining 75,000 elements and converting them to values of '1'.

To get from 25,000 '1' values in the first 25,000 elements in the array (a degree of segregation of 1) to 6250 '1' values in the same number of spaces (the number that would theoretically exist in the first 25,000 spaces in a random population with a '0' degree of segregation and 25% occupied by '1' values) requires removal of 18,750 '1' values. Removal of 20% of these 18,750 values (or 3750) and replacing them in the remaining 75,000 spaces of the array, reduces the theoretical degree of segregation from 1 to 0.8.

The programs written to carry out these sampling studies are somewhat more complicated than those described in the previous section because the populations of the type described in the preceding two paragraphs first had to be defined. For example, the program in Table 24 shows how a population with a degree of segregation of 0.8 is created and sampled. In the 100 DO LOOP section (lines 41-43) the first 25,000 elements of the array are assigned a value of '1', while in the 200 DO LOOP section (lines 45-47) the remaining 75,000 elements are assigned a value of '0'. In the 800 DO LOOP section (lines 50-60) 3750 of the first 25,000 elements are randomly selected and assigned a value of '0', while in the 900 DO LOOP section (lines 63-73) 3750 of the remaining 75,000 elements are converted to a value of '1'.

At this point the sampling operations begin. In the program as written, sampling standard deviations are calculated for approximately 400 randomly located increments apiece for increment sizes 1, 49, 99, 149, ..., 999. Note that after the sampling standard deviation is calculated for each increment size (in the 600 DO LOOP), a new

Table 24: Program for sampling from a population with 25% of a component of interest and $z = 0.8$

```
C   c    This program repeats Visman's original sampling experiment
C   c    for a population in which approximately 21250 lead balls occupy
C   c    the first 25000 locations in the array and the remaining 3750
C   c    lead balls are randomly distributed over the remaining 75000
C   c    locations.  This study is carried out in one dimension as
C   c    opposed to two as carried out by Visman, and uses 100,000
C   c    elements instead of the 10,000 used by Visman.

         Real x(100000), z(400), xavesub(400), r(25000), w(25000)
         Integer seed, y(400), j, jcounter
         Integer seeda, seedb, iw(25000), ir(25000)
         Open(unit=3, file='qmsque', status='new')


         Print*, 'Enter a seed number for sampling.'
         Read*, seed
         Print*, seed
         Print*, 'Enter a seed number for removing 3750 balls.'
         Read*, seeda
         Print*, seeda
         Print*, 'Enter a seed number for replacing 3750 balls.'
         Read*, seedb
         Print*, seedb
         Write(3,1002)
    1002 Format(2x, 'This is the output for program thes12.')
         Write(3,1000)seed, seeda, seedb
    1000 Format(2x, 'Seed:  ', i8, 2x, 'Seeda:  ', i8, 2x, 'Seedb:  ', i8)
         Do 600 inca = 0, 1000, 50
         If(inca.eq.0)then
         incb=inca
         incsize=1
         Else
         incb=(inca-2)/2
         incsize=inca-1
         Endif
         Do 100 i = 1, 25000, 1
         x(i)=1.0
     100 Continue

         Do 200 i = 25001, 100000, 1
         x(i)=0.0
     200 Continue
```

Table 24: (Continued)

```

        jcounter=0
        Do 800 l = 1, 25000, 1
        w(l)=ran(seeda)*24999.0
        iw(l)=ifix(w(l))+1
        If(x(iw(l)).eq.1.0)then
        x(iw(l))=0.0
        jcounter=jcounter+1
        If(jcounter.eq.3750)go to 801
        Else
        Go to 800
        Endif
800     Continue

801     jcounter=0
        Do 900 m = 1, 25000, 1
        r(m)=ran(seedb)*74999.0
        ir(m)=ifix(r(m))+25001
        If(x(ir(m)).eq.0.0)then
        x(ir(m))=1.0
        jcounter=jcounter+1
        If(jcounter.eq.3750)go to 901
        Else
        Go to 900
        Endif
900     Continue

901     j=400
        jcounter=0
        Do 300 k = 1, j
        z(k)=ran(seed)*(100000-incb)
        If(z(k).le.incb)then
        Go to 300
        Else
        Go to 301
        Endif
301     y(k)=ifix(z(k))
        jcounter=jcounter+1
c         Print*, y(k), x(y(k))
300     Continue


        xtotal=0.0
        Do 400 k = 1, jcounter
        xsubtotal=0.0
        Do 401 inc = -incb, incb, 1
        xsubtotal=xsubtotal+x(y(k)+inc)
c         Print*, y(k), (y(k)+inc), x(y(k)+inc)
401     Continue
```

Table 24: (Continued)

```

      xavesub(k)=xsubtotal/incsize

c      Print*, 'The average is:', xavesub(k), incsize
      xtotal=xtotal+xavesub(k)
400   Continue
      average=xtotal/jcounter

      devtotal=0.0
      Do 500 k=1, jcounter
      dev=(xavesub(k)-average)**2.0

      devtotal=devtotal+dev
500   Continue

      stdev=sqrt(devtotal/(float(jcounter)-1.0))
      Print*, incsize, jcounter, average, stdev
      Write(3,1001)jcounter, incsize, average, stdev
1001  Format(2x, 'Number of Samples:  ', i3,
     + 'Increment Size:  ', i4,
     + 'Mean:  ', f9.6, 'Std. Dev.:  ', f9.6)
600   Continue

      checktotala=0
      Do 150 i = 1, 25000, 1
      checktotala = checktotala+x(i)
150   Continue
      checktotalb=0.0
      Do 151 i = 25001, 100000, 1
      checktotalb=checktotalb+x(i)
151   Continue
      Print*, checktotala, checktotalb
      Stop
      End
```

population with a degree of segregation of 0.8 is created. (DO LOOP 800 and 900 are nested in the 600 DO LOOP.) In this way, the increment size-variance relationships cannot be viewed as being specific to a single array but rather apply to all populations created by the mathematical operations shown.

Selection of approximately 400 increments of each size guaranteed that the true sampling variances, σ_s^2, fell within 15% of the experimental variances calculated in this study 95% of the time. This was estimated from the equation giving the 100(1-α)% confidence interval for σ^2:

$$\frac{(n-1)s^2}{\chi^2_{(\alpha/2,\upsilon)}} \leq \sigma^2 \leq \frac{(n-1)s^2}{\chi^2_{(1-\alpha/2,\upsilon)}} \qquad [35]$$

where $\chi^2 = \frac{1}{2}\left[z_\alpha + \sqrt{2\upsilon - 1} \right]^2$

For $\alpha = 0.05$ and 399 degrees of freedom $\chi^2_{a/2} = 455.75$ and $\chi^2_{(1-a/2)} = 345.08$. Therefore $n\text{-}1/\chi^2$ ranges from 0.86 to 1.16. Note that doubling the number of increments collected to 800 from 400 would reduce this range only by 18% to 0.91 from 1.11.

Rather than relying on the selection of a single pair of increment sizes as described in Chapter 3 for oil sands to estimate values for A and B, a linear regression of sampling variance s_s^2 as a function of the reciprocal of increment weight, w, was run for each population. From the equation

$$s_s^2 = \frac{A}{wn} + \frac{B}{n} \qquad [6]$$

it is clear that the slope of this line would be A and the intercept B. Increment sizes of 1, 3, 7, 11, 15 ... 47, 49, 99, 149, ... 999 contributed to these regressions. The sampling data for populations with theoretical degrees of segregation ranging from 0.0 to 1.0 in increments of 0.2 and with concentrations of either 2.5% or 25% are provided in Appendix G. The slopes and intercepts of the variance-increment size regressions along with their uncertainties and the significance levels of replicate experiments, are summarized in Table 25 for the populations containing 2.5% of '1' values and in Table 26 for those containing 25% of '1' values.

In these tables, the experimental degrees of segregation subscripted as Method 1 were calculated by $z = (B/A)^{1/2}$ where B and A were the intercepts and slopes of the lines as defined above. A clear tendency for the experimental degree of segregation to exceed the theoretical degree of segregation exists. The error in the estimate of z increases with increasing segregation.

A review of the original data from Visman's sampling board experiments (11), revealed the same tendency. For a completely segregated population, the sampling constants generated from sets of increments of 1 and 9 units, 1 and 81 units, and 9 and 81 units yielded estimates of z of 1.2, 5.0 and ∞ respectively. For a population

Table 25: Comparison of experimental and theoretical degrees of segregation for a model population consisting of 2.5% of a component of interest

	Degree of Segregation											
	1.0		0.8		0.6		0.4		0.2		0.0	
	T-1	T-2	T-1	T-2	T-1	T-2	T-1	T-2	T-1	T-2	T-1	T-2
Slope	0.0045	0.0090	-0.0026	0.0212	0.0133	0.0178	0.0279	0.0085	0.0120	0.0142	0.0329	0.0201
Uncertainty	0.0083	0.0062	0.0049	0.0063	0.0027	0.0026	0.0014	0.0018	0.0008	0.0005	0.0006	0.0003
Significance	0.59	0.16	0.64	0.00	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Intercept	0.0227	0.0191	0.0145	0.0129	0.0081	0.0080	0.0035	0.0038	0.0008	0.0011	-0.0002	0.0001
Uncertainty	0.0016	0.0012	0.0009	0.0012	0.0005	0.0005	0.0003	0.0003	0.0002	0.0001	0.0001	0.0001
Significance	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0501	0.0669
r^2	0.01	0.06	0.01	0.27	0.44	0.61	0.93	0.43	0.95	0.96	0.99	0.99
$z_{\text{Method 1}}$	2.24	1.45	-	0.78	0.78	0.67	0.36	0.67	0.21	0.28	-	0.07
$z_{\text{Method 2}}$	0.91	0.82	1.09	0.61	0.62	0.56	0.34	0.56	0.20	0.27	-	0.07
$A_{\text{Method 2}}$	0.02718	0.0281	0.0122	0.0341	0.0214	0.0258	0.0314	0.0123	0.0128	0.0153	0.0327	0.0202

Table 26: Comparison of experimental and theoretical degrees of segregation for a model population consisting of 25% of a component of interest

	Degree of Segregation											
	1.0		0.8		0.6		0.4		0.2		0.0	
	T-1	T-2	T-1	T-2	T-1	T-2	T-1	T-2	T-1	T-2	T-1	T-2
Slope	0.0090	-0.0015	0.0778	0.0505	0.1034	0.1223	0.1552	0.1517	0.1667	0.1843	0.1781	0.2005
Uncertainty	0.0121	0.0115	0.0070	0.0069	0.0047	0.0038	0.0021	0.0022	0.0009	0.0012	0.0013	0.0018
Significance	0.46	0.90	0.0001	0.0001	0.0001	0.0001	0.0001	0.0011	0.0001	0.0001	0.0001	0.0001
Intercept	0.1856	0.1861	0.1187	0.1180	0.0663	0.0663	0.0293	0.0297	0.0079	0.0076	0.0003	-0.0004
Uncertainty	0.0023	0.0021	0.0013	0.0013	0.0009	0.0007	0.0004	0.0004	0.0002	0.0002	0.0002	0.0003
Significance	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.22	0.19
r^2	0.02	0.00	0.80	0.63	0.94	0.97	0.99	0.99	1.00	1.00	1.00	1.00
$z_{\text{Method 1}}$	4.54	-	1.23	1.53	0.80	0.74	0.43	0.44	0.22	0.20	0.13	-
$z_{\text{Method 2}}$	0.98	1.00	0.78	0.84	0.63	0.59	0.40	0.39	0.21	0.20	0.13	-
$A_{\text{Method 2}}$	0.1946	0.1846	0.1965	0.1684	0.1697	0.1886	0.1845	0.1958	0.1756	0.1918	0.1784	0.2001

described by $z = 0.25$, the estimates of 0.33, 0.16 and 0.21 were much closer to their true values.

The errors in the estimates of the degree of segregation and, by extension, in the sampling constants could be eliminated almost completely by adopting the relationship:

$$s_s^2 = \frac{A}{wn} + \frac{B}{n}\left(1 - \frac{1}{w}\right) \qquad [36]$$

The degrees of segregation and revised estimates of A based on this relationship are subscripted as Method 2 in Tables 25 and 26. Equation 36 is the rigorous form of the original Visman sampling expression. Visman had concluded, however, that reduction to the form

$$s_s^2 = \frac{A}{wn} + \frac{B}{n} \qquad [6]$$

was justified when w was in a unit of measurement (grams, tonnes, etc.) that contained many elementary particles of the binomial distribution (i.e. particles containing either 0% or 100% of the component of interest).

Note that the elementary particle of the binomial distribution is not necessarily the same as the average particle described by m unless the component of interest is completely liberated from the gangue such as the case of gold nuggets in gravel. In such an application, however, assays of individually sampled increments are likely to form a log-normal distribution so the data would have to be transformed to fit a

Guassian distribution before the Visman relationships could be used.

When w is the same order of magnitude as the elementary particle of the binomial distribution, as occurs on the sampling board or in the arrays studied here, then

$$B = \frac{s_{\mathrm{Sm}}^{2} - \dfrac{A}{w_{\mathrm{Sm}}}}{\left(1 - \dfrac{1}{w_{\mathrm{Sm}}}\right)} \quad \text{or} \quad \frac{s_{\mathrm{Lg}}^{2} - \dfrac{A}{w_{\mathrm{Lg}}}}{\left(1 - \dfrac{1}{w_{\mathrm{Lg}}}\right)} \qquad [37]$$

and

$$A = \frac{s_{\mathrm{Sm}}^{2}\left(1 - \dfrac{1}{w_{\mathrm{Lg}}}\right) - s_{\mathrm{Lg}}^{2}\left(1 - \dfrac{1}{w_{\mathrm{Sm}}}\right)}{\dfrac{1}{w_{\mathrm{Sm}}} - \dfrac{1}{w_{\mathrm{Lg}}}} \qquad [38]$$

where s_{Sm}^{2} and s_{Lg}^{2} are the variances of the transformed data. The fact that a transformation of the data is needed is obvious from Table 25, where the repeatability of the estimates of A, B and z is poor owing to an inability to obtain representative small increments of the population when it contains only 2.5% of '1' values.

To relate this observation to the real system studied in Chapter 3, the sampling constants for Athabasca oil sand remain unchanged when Equations 37 and 38 are used because the theoretical sampling particle size of 20 g is neither 100% or 0% in the component of interest, with the result that w_{Sm} and w_{Lg} both contain a large number of elementary particles of the binomial distribution. The Visman sampling board as well as the arrays used by Gould and Visman and in this work represent the special case of a completely liberated material where the elementary particle of the binomial distribution and the sampling particle are identical. It is for this reason that the *A*-term remains constant regardless of the degree of segregation of the populations described in Tables 25 and 26.

To separate elementary particle effects from physical or sampling particle effects, populations with blocks of consecutive elements in the array were assigned a value of '1'. Size-variance relationships were established for increment sizes ranging from 1 to 999 elements for populations containing 2.5% and 25% '1' values and '1' values divided into either 1, 2, 4, 8, 16, 32 or 64 equally-sized patches. The patches were randomly located in the array so that their occurrence did not fit a cyclic pattern and cause regular fluctuations in the increment-size variance relationship for reasons discussed previously. The data resulting from these sampling experiments are provided in Appendix H. Values for the sampling constants, r^2, and for the segregation constants are summarized in Tables 27 and 28.

Although it is mathematically possible to calculate the slope and intercept of the variance-increment size relationship (see Tables 27 and 28), it is evident from the correlation coefficient, r^2, that the fit is not a good one. This is because for small increment sizes, especially at low concentrations, the variance is proportional to the mean and the

Table 27: Calculation of sampling constants for a patchy population of 100,000 elements containing 2.5% of a component of interest

	Patch size													
	1		2		4		8		16		32		64	
	T-1	T-2	T-1	T-2	T-1	T-2	T-1	T-2	T-1	T-2	T-1	T-2	T-1	T-2
Slope	0.0045	0.0090	0.0139	0.0124	0.0250	0.0118	0.0253	0.0340	0.0293	0.0119	0.0688	0.0677	0.0961	0.1206
Uncertainty	0.0083	0.0062	0.0113	0.0121	0.0106	0.0124	0.0126	0.0126	0.0178	0.0172	0.0319	0.0311	0.0516	0.0800
Significance	0.59	0.16	0.23	0.31	0.03	0.35	0.05	0.01	0.11	0.49	0.04	0.04	0.07	0.02
Intercept	0.0227	0.0191	0.1832	0.1844	0.1826	0.1817	0.1749	0.1766	0.1701	0.1689	0.1484	0.1519	0.1254	0.1239
Uncertainty	0.0016	0.0012	0.0021	0.0023	0.0020	0.0023	0.0024	0.0024	0.0033	0.0032	0.0060	0.0058	0.0097	0.0094
Significance	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
r^2	0.01	0.06	0.05	0.03	0.15	0.03	0.12	0.19	0.08	0.02	0.13	0.13	0.10	0.16
^{z}Method 1	2.24	1.45	3.62	3.86	2.70	3.83	2.63	2.28	2.41	3.76	1.47	1.00	1.14	1.01
^{z}Method 2	0.91	0.82	0.96	0.97	0.94	0.97	0.93	0.92	0.92	0.97	0.82	0.83	0.75	0.71
^{A}Method 2	0.0272	0.0281	0.1972	0.1968	0.2076	0.1941	0.2002	0.2107	0.1994	0.1808	0.2172	0.2196	0.2215	0.2445

Table 28: Calculation of sampling constants for a patchy population of 100,000 elements containing 25% of a component of interest

	Patch size													
	1		2		4		8		16		32		64	
	T-1	T-2	T-1	T-2	T-1	T-2	T-1	T-2	T-1	T-2	T-1	T-2	T-1	T-2
Slope	0.0090	-0.0015	0.0139	0.0124	0.0250	0.0118	0.0253	0.0340	0.0292	0.0119	0.0688	0.0677	0.0961	0.1206
Uncertainty	0.0121	0.0115	0.0113	0.0121	0.0106	0.0124	0.0126	0.0126	0.0178	0.0172	0.0319	0.0311	0.0516	0.0500
Significance	0.46	0.90	0.23	0.31	0.03	0.35	0.05	0.01	0.11	0.49	0.04	0.04	0.07	0.02
Intercept	0.1856	0.1861	0.1832	0.1844	0.1826	0.1817	0.1749	0.1767	0.1701	0.1689	0.1484	0.1519	0.1254	0.1239
Uncertainty	0.0023	0.0021	0.0021	0.0023	0.0020	0.0023	0.0024	0.0024	0.0033	0.0032	0.0060	0.0058	0.0010	0.0094
Significance	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
r^2	0.02	0.00	0.05	0.03	0.15	0.03	0.12	0.19	0.08	0.02	0.13	0.13	0.10	0.16
^{z}Method 1	4.54	-	3.62	3.86	2.70	3.83	2.63	2.28	2.41	3.76	1.47	1.50	1.14	1.01
^{z}Method 2	0.98	1.00	0.96	0.97	0.94	0.97	0.93	0.92	0.92	0.97	0.82	0.83	0.75	0.71
$^{\Lambda}$Method 2	0.1946	0.1846	0.1972	0.1968	0.2076	0.1941	0.2002	0.2107	0.1994	0.1808	0.2172	0.2196	0.2215	0.2445

values appear to describe a negative binomial distribution. Therefore, if the approximately 400 increments selected happen to hit a relatively small number of clusters, s_s^2 is also small. At large increment sizes, the distribution appears more Gaussian.

In Figure 15 variance is plotted as a function of the reciprocal of increment size for a population with a concentration of 2.5% '1' values in an array of 100,000 elements and with those '1' values distributed in random patches of 39, 78 and 156 elements. The significant feature of the variance-reciprocal of increment size curve is the sudden change in the slope of the curve approximately at the point defined by the patch size. The region of the curve below the patch size extrapolates through the origin. In other words, the model populations successfully predict that at $w = \infty$, ${s_s}^2 = 0$ and not B/n as predicted by the general Visman equation.

A later discussion by Visman and Duncan [14] gives the equations:

$$s_s^2 \sim dp(1 - dp) \text{ for } w = 1 \qquad [39]$$

$$s_s^2 \sim d^2p\ (1 - p) \quad \text{for} \quad 1 \quad w \le P \qquad [40]$$

and

$$s_s^2 \sim d^2p\ (1 - p)\ P/w \quad \text{for} \quad w > P \qquad [41]$$

where p is the frequency of patches in the population (i.e.

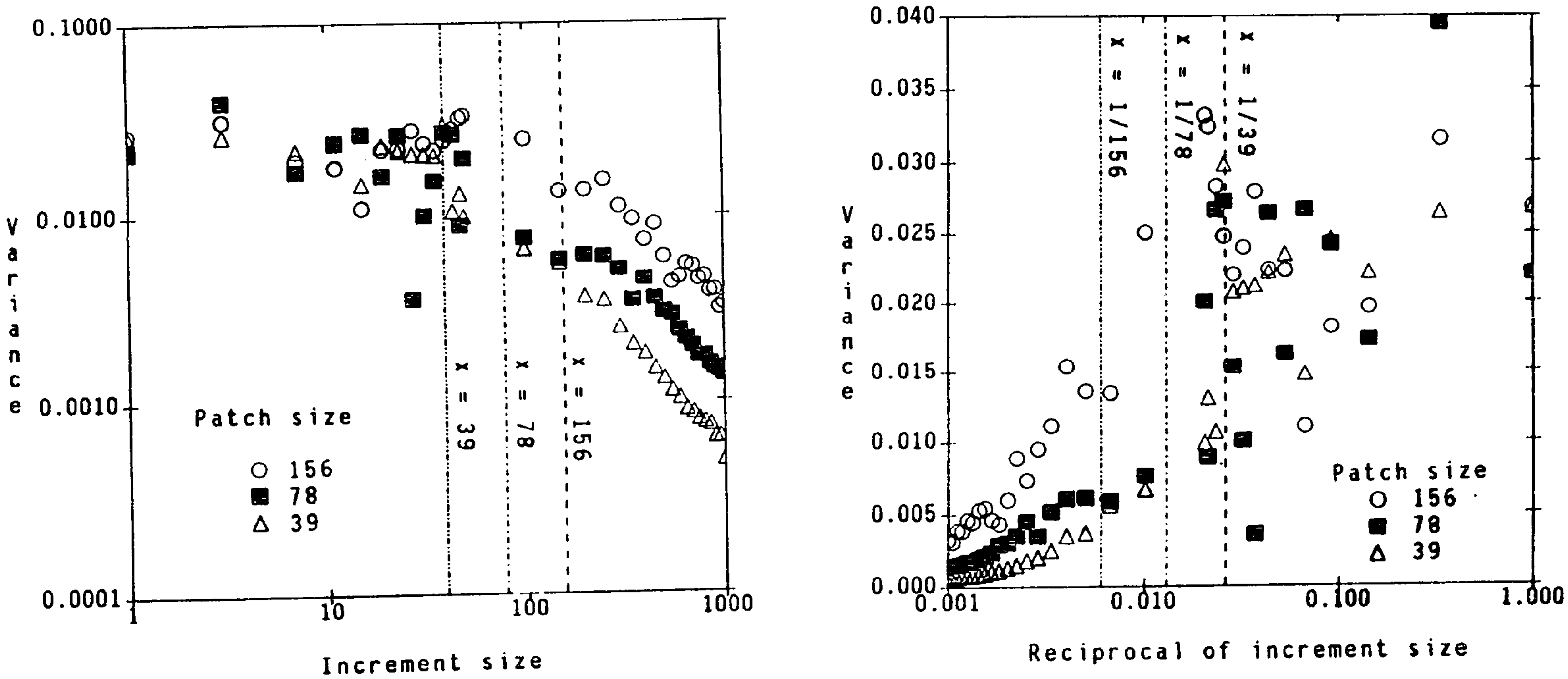

Figure 15. Relationship between increment size and sampling variance for segregated populations with distinct patches.

ΣP/population size), P is the patch size in elemental units and d is the fraction of elemental units in the patch.

As a first approximation, these equations predict variances as a function of increment size. The fourteen tables in Appendix H provide comparisons of experimental variances and variances predicted by Equations 39 to 41. The discontinuous functions for s_s^2 are least precise in the region of $w = P$. Note also that when the increment size exceeds the patch size, as described in Equation 41, sampling variance is inversely proportional to increment size, which is the same as the relationship for well-mixed populations. This is clear proof that the degree to which a population appears to be segregated is a function of increment size.

We now have empirical evidence that the general sampling equation:

$$s_s^2 = \frac{A}{wn} + \frac{B}{n}$$

is applicable for predicting sampling variance for different increment sizes in Athabasca oil sand but is not applicable for populations containing a negative binomial distribution of the component of interest. The fact that Equation 6 does work for oil sand, while Equations 40 and 41 do not, is clear proof that sampling boards and arrays, as described in Visman's and in this work, oversimplify the distribution of components in some populations. Real patches are not always sufficiently distinct and homogeneous in size to permit adequate simulation.

It is clear that of the general equation of Visman for "patchy" populations (seeds in a field, moulds in a culture or in food) is inappropriate for predicting sampling variance and that alternatives exist for these situations as given in Equations 39 to 41. It is also evident that some prior knowledge of the nature of a population is prerequisite to predicting sampling variance. This can be accomplished only through collection of a variety of sets of increment sizes (three being the minimum) over the potential range of sizes that may be collected in future studies of that type of population.

5.4 Conclusions

1. A one-dimensional array can be used to successfully model the sampling variance that will occur when sampling real-life populations if the element of interest appears in the form of a binomial distribution or in distinct patches of a consistent size (i.e. a negative binomial distribution). This array is much simpler to program than the two-dimensional arrays used by Visman and Gould and yet yields the same qualitative results as these more complex arrays.

2. The general expression describing sampling variance is limited to cases where patches of the component of interest are not well defined, and where the increment size is smaller than the average "patch" size but larger than the elementary particle size of the

population (i.e. the particles are either 100% pure or completely devoid of component of interest).

3. It is possible to envision cases where any one of three "constituents" of a population may control sampling variance. For example, in ion-microprobe analysis and certainly mineral identification in electron-microscopy where the elemental composition is determined at very small sampling locations, elementary particle size and the statistics of the binomial distribution control sampling variance. In both coal sampling, where the physical dimensions of a particle or lump and can be measured, and in oil sand sampling at the 50 to 1000 g level, the average particle mass controls sampling variance. Patch size may be the important element in the analysis of cores where the length of increment taken generally exceeds the size of the average stratum in the deposit. In all cases, it is important that there is no well-defined cyclic pattern in the population.

4. To understand the nature of the population being sampled, while at the same determining sampling constants, collection of sets of increments over a wide size range is preferable to collecting either pairs of increments of one size or two sets of increments varying by about a factor of 10. If the two-increment size approach for calculating A and B is used, the recommendation in Chapter 4 that w_{Lg} be at least $10w_{\mathrm{Sm}}$ should be followed, but the difference between w_{Lg} and w_{Sm} should not be so large that there is

a possibility of passing from a patch-controlled to a particle-controlled area of the sampling variance-increment size relationship. In the absence of a clear understanding of the nature of the population being sampled, extrapolation of the sampling variance outside of the increment sizes used to define the sampling constants is not recommended.

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APPENDIX A

Sampling for Chemical Analysis

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Analytical Chemistry 1981,
53(8), 924A-938A.

Sampling for Chemical Analysis

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As analytical methodology improves and instrumental methods allow, or often require, the use of smaller and smaller analytical test portions, the error in the sampling operations becomes increasingly significant. Also, heterogeneity of trace components can introduce major sampling problems. Sampling errors cannot be controlled by use of blanks, standards, or reference samples and so are best treated independently. A goal of this review is to make analysts aware of the uncertainties introduced into analytical measurements during sampling and of the work that has been done in recent years to aid in identifying and reducing these uncertainties. The practical importance of the subject is shown by the large number of sampling protocols written by a variety of standards organizations.

This review covers about the last 8 years of work in the area of sampling for chemical analysis. Most of the references were obtained by a computer search of Chemical Abstracts, Biological Abstracts, and American Petroleum Institute Abstracts for the period January 1975 to November 1983. Also included are a few references obtained from other sources, some of which are older than 1975 but are considered significant enough to include in a one-time review. The topic was included in the fundamental review on Statistics in 1972 by Currie, Filliben, and DeVoe (*106*), and some coverage was provided in the reviews on Chemometrics by Kowalski in 1980 (*261*) and by Frank and Kowalski in 1982 (*155*).

Terminology in the area of sampling is often used in different ways by statisticians, chemists, and others. Therefore a short table of definitions is provided (Table I). These definitions have been selected to be compatible insofar as feasible with those recommended by various standards organizations.

The review has been organized under the headings general considerations, theory, and standards, followed by applications in the areas of mineralogy, soils, sediments, metallurgy, atmosphere, water, biology, agriculture–food, clinical–medical, oil–gas, and miscellaneous. A few papers not strictly related to chemical systems are included because they provide concepts or approaches that may be applicable to chemical problems. Also, several significant older papers have been included for completeness. Acceptance sampling, though important in its own right, has not been included. The reader interested in this area may consult as a beginning ref 125.

Sampling devices and their proper use are also important. Analytical data are critically dependent on the nature of the samples and this often depends on the way in which they are obtained. Considerable attention has been given to the design of samplers that can operate reproducibly and which do not compromise the sample in any significant way.

GENERAL CONSIDERATIONS

The focus of chemical analysis has gradually enlarged with time to encompass the solution of a problem represented by a sample rather than simply a determination of sample composition (*194*). To achieve this goal analytical chemists must understand sampling theory and practice as well as measurement procedures. Many authors have addressed this general issue (*22*, *193*, *203*, *220*, *381*, *493*).

Youden considered sampling to be a possible major source of error in the analytical process (*532*). He emphasized the importance of being able to place confidence limits on a result and that obtaining only a single result from a composite sample is of little value unless the variability of the parent population and analytical methodologies are known from extensive prior experience. As a guideline, he proposed that when the analytical error is one-third or less of the sampling error, further reduction of the analytical error is not important.

While addressing concerns in environmental sampling, Ku stated that a prerequisite to the development of an efficient analytical strategy is definition of the purpose for which the results are going to be used (*268*). The ACS Committee on Environmental Improvement has further developed this point with respect to both sampling and analysis (*1*). The Committee recommended that an acceptable sampling program should at least include (1) a proper statistical design which takes into account the goals of the studies and its certainties and uncertainties, (2) instructions for sample collection, labeling, preservation, and transport to the analytical facility, and (3) training of personnel in the sampling techniques and procedures specified. These points should be applied to all analyses.

A number of general interest reference books include material on sampling considerations and elementary statistical principles in the overall analytical process (*22*, *37*, *42*, *53*, *99*, *112*, *123*, *210*, *248*, *272*, *297*, *475*, *496*). The book on bulk sampling of chemicals by Smith and James (*443*) covers the theory and practice of sampling items of commerce which occur in well-defined populations such as consignments, batches, or stock piles. The book by Williams (*523*) provides a readable discussion of sampling theory that includes many examples, particularly from social and financial sources. The papers from a symposium on sampling, standards, and homogeneity have been published as a book by ASTM (*8*). The scope is broad, from sampling the moon, to collecting physical evidence for a forensic laboratory, to sampling of regions in the discharge gap of a spark source emission spectrometer.

Reviews by Bicking addressed the sampling of bulk materials in terms of physical and statistical aspects (*52*, *53*). The earlier review is useful on an introductory level; it gives examples of calculations to determine optimum sample size, number of samples, cost, and errors arising from the various stages of an analytical process (analysis of variance). The more recent one emphasizes apparatus and techniques. A discussion by Kratochvil and Taylor (*264*) summarized the place of sampling in analysis and reviewed the more important sampling theories. Zar has outlined calculations for determination of the number of samples required to test various statistical hypotheses (*536*).

A selective annotated bibliography contains 115 references on general sampling considerations and applications to agricultural products, the atmosphere, gases, water, and wastewater (*265*). A number of these references are earlier than the time period covered by this review. Sampling, sample handling, and storage for environmental materials have been

Table I. Glossary of Terms Used in Sampling

Bulk sampling.	Sampling of a material that does not consist of discrete, identifiable, constant units, but rather of arbitrary, irregular units.
Gross sample.	(Also called bulk sample, lot sample.) One or more increments of material taken from a larger quantity (lot) of material for assay or record purposes.
Homogeneity.	The degree to which a property or substance is randomly distributed throughout a material. Homogeneity depends on the size of the units under consideration. Thus a mixture of two minerals may be inhomogeneous at the molecular or atomic level but homogeneous at the particulate level.
Increment.	An individual portion of material collected by a single operation of a sampling device, from parts of a lot separated in time or space. Increments may be either tested individually or combined (composited) and tested as a unit.
Individuals.	Conceivable constituent parts of the population.
Laboratory sample.	A sample, intended for testing or analysis, prepared from a gross sample or otherwise obtained. The laboratory sample must retain the composition of the gross sample. Often reduction in particle size is necessary in the course of reducing the quantity.
Lot.	A quantity of bulk material of similar composition whose properties are under study.
Population.	A generic term denoting any finite or infinite collection of individual things, objects, or events in the broadest concept; an aggregate determined by some property that distinguishes things that do and do not belong.
Reduction.	The process of preparing one or more subsamples from a sample.
Sample.	A portion of a population or lot. It may consist of an individual or groups of individuals.
Segment.	A specifically demarked portion of a lot, either actual or hypothetical.
Strata.	Segments of a lot that may vary with respect to the property under study.
Subsample.	A portion taken from a sample. A laboratory sample may be a subsample of a gross sample; similarly, a test portion may be a subsample of a laboratory sample.
Test portion.	(Also called specimen, test specimen, test unit, aliquot.) That quantity of material of proper size for measurement of the property of interest. Test portions may be taken from the gross sample directly, but often preliminary operations such as mixing or further reduction in particle size are necessary.

described by several authors (*51, 173, 183, 300*). Sampling for pesticides (*144, 151*) and polyaromatic hydrocarbons (*494*) in a variety of environments has been reviewed. Reviews of a more specific nature are referenced in the appropriate sections.

THEORY

This section considers in an abbreviated way developments in sampling theory over the past several years. The application of statistical methods to sampling for chemical analysis is relatively common, but most work has aimed toward the solution of specific types of problems, and with few exceptions little has been done on more unified approaches.

For a detailed treatment of general statistical sampling theory the book "Sampling Techniques" by Cochran is the best (*101*). Although the focus tends toward sample surveys, such as obtained from census data or public opinion polls, most of the material can be applied to chemical problems.

In sampling for chemical composition four workers, Gy, Ingamells, Visman, and Benedetti-Pichler, have made especially significant contributions to general statistical sampling theory. Each has emphasized different aspects of the problems. All four work in the area of geochemical or mineral evaluation.

Pierre Gy, a consulting engineer, has studied the sampling of granular materials, especially in streams in mineral beneficiation or extraction plants. The book "Sampling of Particulate Materials, Theory and Practice" (*189*) summarizes years of study. According to Gy the sampling of a heterogeneous material containing a small quantity of a sought-for substance depends on particle shape, particle size distribution, the composition of the phases comprising the particulates, and the degree to which the substance sought is liberated from the remainder of the material (gangue) during particle size reduction by grinding or crushing. He defined factors f, g, c, and l for these four effects. The shape factor f is the ratio of the average volume of all particles having a maximum linear dimension equal to the mesh size of a screen to that of a cube which will just pass the same screen. Thus $f = 1.00$ if all particles are cubes and 0.524 if they are all spheres. For most materials f can be assumed to be 0.5. The particle size distribution factor g is the ratio of the upper size limit (screen size through which 95% of the particles pass) to the lower size limit (screen size through which 5% of the particles pass); $g = 1.00$ if all particles are the same size. The composition factor c is given by

$$c = \frac{1-x}{x}\,[(1-x)d_x + xd_g]$$

where x is the overall concentration of the component (mineral) of interest and d_x and d_g are densities of the component of interest and the remaining material (gangue). The value of c can range from 0.05 g/cm^3 for a high concentration of c to 10^6 or greater for trace concentrations. The liberation factor l is defined as $l = (\text{diameter}_1/\text{diameter})^{1/2}$, the square root of the ratio of diameter of the average grains of sought-for component in the material divided by the diameter of the largest particles in the mixture. The value of l approaches 1.00 as particle size approaches grain size.

Once these four constants have been estimated, the sampling variance s^2 in a sample of weight w can be estimated by

$$s^2 = fgclu^3/w$$

where u is the linear dimension of the largest particles. Alternatively, the sample weight required for any desired uncertainty level can be calculated.

Gy has also considered in a systematic way all the potential sources of error in sampling. He includes effects due to the nature of the material being sampled, to treatment of the material after collection, to the physical sampling operation, and even to deliberate bias introduced by the sampler (fraud). Some sampling problems cannot be treated statistically.

Ingamells has also contributed in a major way to the development of sampling theory. With Switzer (*233*) he proposed a sampling constant K_s that permits estimation of the subsampling error when withdrawing a small portion of a well-mixed material. The weight w of sample which should be taken to give a sampling relative standard deviation of 1% at the 68% confidence level is given by $w = K_s/R^2$, where R is the relative standard deviation, expressed in percent, found experimentally for the material. Ingamells' constant is best estimated by measurements on sets of samples of several different weights (*228*).

Ingamells' constant is related to the Gy equation by $K_s = fgcl(u^3 \times 10^4)$; it shows that the individual factors of Gy do not need to be determined to establish a relation between sample weight and sampling uncertainty for well-mixed materials (*230*).

Ingamells derived the sampling constant expression by assuming that the sampling characteristics of a bulk material for a given component can be duplicated by considering the material to consist of a mixture of uniform cubes of two kinds of particles, one containing P_1% and the other P_2% of the component of interest. He showed that for heavy metal ores $K_s = 10^4(\bar{P} - P_1)(P_2 - P_1)u^3d_2/\bar{P}^2$, where $\bar{P}$ is the overall percentage of the sought-for component in the sample, d_2 is the density of the particles containing P_2 percent, and u^3 is the volume of one of the cubes (*231*). It is important to recognize that in the derivation of this constant a well-mixed population, that is, one in which segregation is not present, is assumed.

Scilla and Morrison (*415*) applied the concept of a sampling constant to the in situ microsampling of solids by the ion microprobe. Their approach allowed the degree of heterogeneity of the solid to be estimated, and procedures for obtaining the practical number of replicate analyses required to achieve a desired precision were proposed. The method was verified by using NBS SRM low alloy steels. A significant point made by these authors was that analytical measurements on heterogeneous samples with a probe only a few micrometers in diameter may yield unrealistically high precision and erroneously low concentrations if the number of inclusions containing high concentrations of the constituent of interest is low. In this case a set of replicate measurements may reflect the concentration of the constituent in the matrix, with an occasional high result which in other circumstances would be considered an anomalous outlier but which may in reality arise from the probe sampling an inclusion.

Visman (*488*) has developed a general theory of sampling that takes into account the effects of heterogeneity in both well-mixed and segregated populations. On the basis of an experimental evaluation of sampling standard deviations of items on a sampling board for random and various segregated distributions, he proposed that the sampling variance s_s^2 could be related to individual increment size w and number of increments n by

$$s_s^2 = \frac{A}{wn} + \frac{B}{n}$$

The constant A is called a homogeneity constant and is related to Ingamells' subsampling constant K_s and the average composition of sought-for component by $A = 10^4 \bar{x}^2 K_s$. It is a function of the total weight of sample collected. The constant B is called a segregation constant. Values for A and B can be obtained experimentally for a bulk population in two ways. In the first way two sets of samples are collected, one with w as small and the other as large as feasible. The increments are analyzed and two sampling variances calculated. From the two equations the values of A and B can be obtained.

A second approach arises from a series of published discussions of Visman's original paper by Duncan and Visman (*124, 489, 490*). Duncan pointed out the similarity between the segregation concept of Visman and clustering as defined by statisticians. Visman then proposed that values for A and B be obtained by collecting a series of pairs of increments from the population, each member of a pair being of the same weight w and collected from nearby sites in the bulk. From analyses of the increments an intraclass correlation coefficient r is calculated (*446*). Values for A and B are then calculated from the Visman equation and the relation $r = B/Am$, where m is the reciprocal of the average particle mass. A value for r can also be calculated by conventional ANOVA (*447*). The Visman method has been recommended for sampling of coal (*172*).

Benedetti-Pichler (*42, 43*) pointed out some years ago that random sampling error may occur even in well-mixed particulate mixtures if the particles differ significantly in composition and only a small number are taken for analysis. He considered the bulk material as a two-component mixture, with each component containing a different percentage of the analyte. The number of particles n required to hold the relative sampling standard deviation (sampling uncertainty) R in percent to a preselected level may be calculated from the relation

$$n = \left[\frac{d_1 d_2}{\bar{d}^2}\right]^2 \left[\frac{100(P_1 - P_2)}{R\bar{P}}\right]^2 (p)(1 - p)$$

where d_1 and d_2 are the densities of the two kinds of particles, $\bar{d}$ is the average density of the sample, P_1 and P_2 are the percentage compositions of the component of interest in the two kinds of particles, $\bar{P}$ is the overall average composition in percent of the component of interest in the sample, and p and $1 - p$ are the fractions of the two kinds of particles in the bulk material. Once density, n, and particle size are known, the weight of sample required for a given level of sampling uncertainty can be obtained. For example, assuming spherical particles, the minimum sample weight is given by $(4/3)\pi r^3 n\bar{d}$. Alternatively, for a prespecified sample weight the extent of grinding necessary to increase n to a value corresponding to any selected sampling uncertainty can be determined. If particles of varying size are present in the mixture, the largest particles should be considered to control the sampling uncertainty, and the calculations should be based on their diameter. Applications of the method to the preparation of reference samples (*204*) and to other systems (*203, 263*) have been considered. Benedetti-Pichler provided some guidelines for approximating a mixture of several kinds of particles as a two-component system (*42*).

Brands (*65*) has developed equations for estimating the variance in sampling of inhomogeneous particulate materials by a statistical treatment based on particle size, number, and composition. Multicomponent mixtures are handled by summing the contributions of the various particle types and sizes. Calculated sample sizes for all particulate materials are sensitive to particle shape. This is because most particles tend toward rough spherical shapes (*190*) and the volume of a sphere of diameter d is only a little over half the volume of a cube of side d. Brands (*66*) extended the system to segregated substances and derived equations for three different sampling patterns—one increment, several increments, and a composite of several increments. He concluded that a general strategy for sampling cannot be given. Accuracy of sampling can only be improved by use of prior knowledge of the system.

Ellis (*136*) has proposed a quantity termed the theoretical grain index (TGI) as an indicator of segregation of the analyte in sampling of powders. The TGI is defined as the average number of theoretical grains composed of 100% analyte per gram of sample; it is calculated by $\mathrm{TGI} = 10^{-12} F U^{-3}$, where F is the fraction of analyte in the sample and U is the diameter of the largest grains (given by the smallest sieve opening in μm that passes all the sample). A value for the product of TGI times test portion weight in grams that is greater than 200 indicates possible error from analyte segregation; values below 200 indicate little risk of error due to segregation. The paper includes a convenient table of sieve mesh numbers and apertures in μm for four different sieve series (U.S. Standard ASTM No. E11, Tyler, British Standard BS-410, and South African Standard SABS-197).

Ranked set sampling employs ordering by judgment of a set of *n* randomly collected increments to obtain an estimate of an average (*116*). In each set all increments are ranked visually or by any rapid, simple means not requiring assessment of actual values, and the lowest ranked is analyzed. A second independent set is then collected from the population and ranked as before and the second lowest ranked increment is analyzed. The operation is repeated on *n* sets, and the average of the *n* analyses taken. This average may be known with greater precision than for *n* analyses done on random increments if the ranking is reasonably accurate and the population has a unimodal distribution. The method may be useful in a number of analytical applications where a visual or simple scanning method allows rapid ranking.

The theory of point sampling was related to earlier standard single-stage cluster sampling theory by Schreuder (*410a*). Point sampling is a special type of classical cluster sampling, and is useful for such problems as sampling of trees on a tract of land. Little has been done in applying this approach to chemical problems.

Royall (*396a*) has concluded that for some models systematic (nonrandom) sampling plans are better than random ones. The role of randomization in sampling plans is important but not well understood by many experimenters. In many instances it is both more convenient and less costly to sample in a systematic fashion, and the loss of information incurred because some probability estimates cannot be made may not be great enough to be a deterrent. Systematic sampling has been shown by Visman (*488*) to be as effective as random sampling in providing estimates of variance for a variety of sample sizes and population distributions in which periodicity is absent. Cochran (*100*) showed that systematic sampling compares favorably in precision with stratified random sampling but may give poor precision when unsuspected periodicity is present. Also, with systematic sampling no trustworthy method is known for estimating the variance of the population from the sample data. In general, systematic sampling tends to give about the same precision as random sampling for most populations but is easier and less prone to error during sample collection.

The variance between batches of material fed to a blender and the variance of the blends produced have been derived by Bourne (*61*) for cases where the feed batches are independent and where they are serially correlated. The resulting equations were applied to four different blending procedures—sequential, selective, random, and semicontinuous. Correlation between batches strongly influences the proportion of blends falling within specified limits, positive correlation lowering the proportion of satisfactory blends and negative correlation increasing the number. The related problem of sampling of lots which show internal correlation was considered by Muskens and Kateman (*338*), who studied a production line or conveyor belt carrying material in which the component of interest varied in concentration with time. They concluded that the best strategy is to collect a sample over the whole time period and analyze it by a method of high precision. If a single composite sample cannot be collected, or if a precise analytical method is not available, the number of samples must be increased to yield a specified level of uncertainty.

Coulman (*104*) has considered chemical sampling as a data filter. A discrete sample removed from a flowing stream that is varying in composition with time yields mean composition over the time of sampling. Modification of this integral mean by varying the sampling rate with time allows filtering out of noise in the system when the sampling rate is a sine or cosine function and a sufficiently low sampling frequency is employed. The approach was successfully applied to a computer model of two continuously stirred chemical process tank reactors.

Rohde (*389*) has discussed in a general way the advantages of compositing when testing for the presence of a seldom occurring property such as a low level of a contaminant in a chemical product, or pesticide residues in produce or meat products.

Brown and Fisher (*76*) have derived equations for estimation of the variance of the mean for composited samples from discrete units such as bales of wool or bags of grain. Three contributions to the overall variance are identified: σ_a^2, the variance in the proportion of any single sample increment from the composited sample ending up in a given subsample; σ_b^2, the variance between the units (between bales); and σ_c^2, the variance within units (within bales). The first of these has been overlooked previously; ways in which it can be estimated are suggested. Experimental verification of the equations was not provided.

Approaches to the theory of successive sampling for ratio and regression estimators involving use of information from the first of two sampling occasions on two auxiliary variables have been studied by Sen (*421*).

Theoretical work on sampling of biological materials such as forests for trees, lakes for fish or algae, the atmosphere for particulate or gaseous pollutants, and so on is meager. The sampling of large objects such as herds of animals or forests has been treated by Jolly (*244*). The surface on which the objects are located may be divided into sampling units of different types, such as irregular shapes, strips of fixed width, or line transects. Subsamples may be taken from the sampling units. The method should be applicable to a variety of chemical analytical problems, such as sampling surfaces with microprobe devices or mineralogical exploration.

Some general guidelines of utility to workers in specific areas are being developed; these are included under the appropriate subheadings in subsequent sections.

STANDARDS

A large volume of literature has been provided by various associations on sampling of materials in trade and commerce. These include standard procedures for dealing with specific materials, as well as general guidelines. Examples of the latter category are those by the American Society for Testing and Materials (ASTM) on Standard Recommended Practices for sampling industrial chemicals (*3*), for choice of sample size to estimate the average quality of a lot or process (*5*), for probability sampling of materials (*4*), and for acceptance of evidence based on the results of probability sampling (*6*).

Many standard procedures for sampling and for the design and use of sampling devices, particularly for industrial analysis, are contained in the ASTM Book of Standards. The reader interested in the analysis of such materials should consult the latest index, published annually (*9*), for references to procedures recommended by concensus action of users. Other associations that provide similar information have been tabulated by Walton and Hoffman (*496*); an updated list would likely include many more. Other countries provide standard methods that are often different from those established in the U.S. Thus Japan has an industrial standard covering general rules for methods of sampling of bulk materials (*237*), and Britain has standard methods for sampling chemical products (*75*). Varying standards cause difficulties in international trade, and so standards acceptable to many nations are being developed by the International Standards Organization (ISO). Work on a variety of ISO standards relating to sampling for chemical analysis is well under way.

MINERALOGY

The sampling theories outlined earlier have their foundations in mineralogical sampling, particularly in the subsampling of ores in the laboratory (Ingamells and Benedetti-Pichler) and in commercial bulk applications (Visman and Gy). These contributions will not be discussed further here. Harnby considered the precision of estimates of the mean and standard deviation in particulate mixtures (*199*) and applied social survey statistical techniques to the analysis of particulate mixtures (*200*). Using a coefficient of correlation which expresses the degree of correlation between neighboring particles in a mixture, he established a relationship which can be used to predict the between-sample variance as sample size is varied for a variety of mixture models. Kristensen defined the variance between samples as a function of mean particle weight, particle densities, proportions of the components, sample size, and coefficient of correlation for random and nonrandom (segregated) mixtures (*266, 267*). Sampling plans for evaluation of kyanite in ceramic raw material were evaluated by Hackler and co-workers (*191*). The variability at each stage of sampling was estimated and subjected to an analysis of variance so as to optimize cost and work factors. Advantages and disadvantages of composite sampling were discussed.

Wilson (*525*) concluded that for most powdered and well-mixed silicate rocks a 1-g sample of 72-mesh powder is suitable for determination of the major elements. He found, as expected, that trace elements forming characteristic minerals are subject to greater relative sampling error than those contained in major mineral species. He also showed that for powders of uniform grain size the variance is inversely proportional to the number of particles sampled, but for varying particle size the variance is inversely proportional to the number of particles per gram of material (weighted reciprocal mean). A statistical expression relating the size and number of gold particles in a powdered material containing little gold with the measurement variance has been derived (*460*). Comparison of calculated subsample sizes with those estimated by the subsampling approaches of Ingamells and Wilson was fairly good.

Kleeman recommended that rock samples for analysis should be crushed to pass a 120-mesh sieve and 0.5-g test portions should be analyzed. Reference samples should pass a 230-mesh sieve (*256*). Other investigations of the sampling of powders have been reported for the determination of uranium (*269*) and K–Ar dating of biotite (*137, 232*). Ingamells has presented sampling demonstrations by using grains of dolomite and silicon carbide to illustrate the principles of sampling of ores in the laboratory. A miniature vertical milling machine for routine use to obtain microsamples of sedimentary rock components is described by Prezbindowski (*378*).

Although reduction of the laboratory sample to test portions can be a significant source of analytical error, obtaining laboratory samples which represent the parent population presents a much greater problem. Schultz's reviews on solid and gaseous fuels have addressed the problems of sampling coal, coke, and natural gases (*414*). Visman developed his sampling theory for the purpose of describing commercial shipments of coal (*488*). Both ASTM (2) and the American Pulp and Paper Institute (*21*) have developed standards for sampling coal. Argonne National Laboratory is preparing a series of premium coal samples for research purposes (*192*). These will be protected from oxygen during collection and preparation to retain their original chemical composition. Bennett showed that the medium-size fractions taken from a stock pile of chrome ore were more representative than either the fine or coarse fractions (*44*). Carley demonstrated that sampling and subsampling procedures for coal should not be applied indiscriminately to oil shale. The special characteristics of oil shale had to be considered to determine optimum sampling schemes (*87*). In mining applications Ingamells observed that histograms of metal concentrations from exploration data are often skewed (*229*). If the skew can be attributed to large-scale gradation in ore composition, a geostatistical evaluation is indicated. However, if the skew is due to the nugget effect (the presence of occasional test portions of high analyte concentration), a different approach must be taken. In its simplest form, Ingamells' equation for determining the true grade of an ore is $K = Y + (Y - L)/2Z$ where K is the overall grade of the ore, Y is the mode of a set of samples, L is the grade of the ore without nuggets and Z is the fraction of samples assayed which contain nuggets.

Maxwell (*312*) discussed sampling and sample preparation at the Geological Survey of Canada. Sandu used geostatistical, statistical, informational, and analytical methods to determine the required testing interval in a vein polymetallic deposit (*403*). The optimum testing interval for the deposit under examination was 5 m. Zwicky (*540, 541*) used the geostatistical principles of Matheron (*310*) to determine if the sampling pattern followed in the exploration of a lease in the Athabasca oil sand deposit was sufficient to evaluate the lease in terms of oil sand grade and net pay. The data indicated that the radius of influence for a given core hole was approximately 1300 m. Thomas analyzed SO_2 production data from a coal mine and showed that geostatistical principles may be applicable to coal deposit sampling (*471*). Santo Oliveira prepared an introductory paper describing sampling and analytical errors in geochemical prospecting (*406*) and Switzer discussed statistical methods as applied to other sciences using simple examples (*466*). The contamination of well cuttings by drilling mud (*129*) has been addressed.

A core boring machine was developed by Daube (*111*) to make exploratory drillings in carbonate rock. The use of the machine in evaluating the quality of minerals was discussed.

SOILS

Sampling soils for nutrient content is a concern to many. James and Dow reported that soil variability can be categorized in three ways: (1) microvariation, the variability between points in the soil separated by fractions of an inch; (2) mesovariation, the variability between points separated by up to a few feet; and (3) macrovariation, the variability between points separated on a scale larger than a few feet (*236*). Their studies on soil fertilization clearly illustrated variations on the three scales. Microvariation was attributed to the zone of influence of a single fertilizer pellet, mesovariation to the mechanical application of the pellets, and macrovariation to the natural soil properties. They proposed a modified point sample system in which a cluster of samples are taken at each point. Random sampling schemes provide estimates of a mean and confidence limits but may not provide adequate patterns of soil fertility. Therefore, to determine macrovariation most efficiently, systematic sampling was recommended by James and Dow. In a review of soil sampling Petersen and Calvin pointed out that an exception to this recommendation may occur if systematic sampling is used when the population has a periodic trend (*365*). In such a situation, knowledge of the period of the trend allows modification of the systematic sampling so the sampling interval is equal to an odd multiple of the half period.

Tonark-Ngarm reported that stratified sampling provides a reliable estimate of the mean with the least number of chemical analyses (*476*). While this statement in a narrow sense may be true, these authors believe that when the sampling and analyses required to identify the strata are considered, stratified sampling in soils is not an efficient approach.

Recommended field sampling schemes for a variety of nutrients in forest and agricultural settings have been reported (*163, 257, 377, 383*). Measurements of soil gases can be accomplished by collecting samples for later gas chromatographic measurements (*80*) or can be conducted on-site with a portable probe and mass spectrometer (*393*).

Taylor and co-workers determined that relative uncertainties of soil dieldrin (pesticide) analyses cannot be reduced below 20% at practical sampling rates (*468*). The complete analytical scheme including sampling, storage, and analysis of a fungicide in soil has been described (*374*).

Sampling schemes for soil mapping and classification studies have been reported. Edmonds evaluated long and short range soil variation plus sampling and analytical errors for mineralogical components of soil (*132*). Webster determined the required sampling intervals for a variety of properties such as pH, bulk density, and water, phosphorus, and potassium content at an experimental station in Australia (*500*).

Analysis of soil for residues and for the distribution of contaminants requires a large number of samples to be taken, often over an extended area. Several mechanical devices have been developed to facilitate such sampling. Apperson and co-workers (*24*) describe a sampling device for taking small plugs of soil, and discuss its use in the determination of pesticide residues. Ivancsics (*235*) has developed a new mechanical soil sampling machine equipped with disks, drawn by a tractor. Specially designed spoons on the disks take samples out of the soil at a given depth. The use of two disks allows collection of parallel samples. A three-wheeled self-propelled soil sampler accomplishing similar results has been described by Smith and co-workers (*441*). Robertson and Bracewell (*393*) discuss the use of a portable field probe for sampling soil gas compositions. The question of in situ analysis as compared to laboratory samples for mapping ^{241}Am and ^{239}Pu soil concentrations is addressed by Kirby and co-workers (*253*). An array of four high-purity, planar, Ge detectors provided soil concentration contours with confidence intervals that were one-third as wide as those obtained by soil sampling. Silkworth and Grigal (*433*) conducted a study of in situ soil solution samplers and found 5-cm diameter porous ceramic cups to be better than fritted glass or hollow cellulose fibers. Considerations in designing a remote-controlled soil sampler have been discussed by Alic (*18*). The cost of the sampler precludes it from most commercial applications; the sampler was designed for use on the Viking mission to Mars.

METALLURGY

The introduction of instruments such as the ion microprobe and secondary-ion mass spectrometer (SIMS), which provide analytical information from square micrometers of surface, and techniques such as analytical electron microscopy, electrothermal atomic absorption, and proton-induced X-ray emission (PIXE), which require samples of less than a milligram, has resulted in the analytical error often becoming insignificant relative to sampling error. The sampling problem in this context requires specification of minimum test portion sizes for primary standard reference materials, which often precludes their use with techniques that accept only small sample quantities.

Morrison applied the sampling constant concept as a measure of variability on the microscale. An early calculation of a sampling constant K_s neglected the distribution of volume, shape, and density of the inclusions in which most of the impurities were assumed to be found (*415*). In a subsequent study using digital processing of the image he reported that a sampling constant could be evaluated considering the variability in the above factors (*142*). The sampling constant was defined as

$$K_s = (1/I_T)(A_T \sum_{i=1}^{N} i_i^2)^{1/2}(1 - A_I/A_T)^{-1/2}$$

where K_s is the sampling constant in micrometers, i_i is the intensity of inclusion i, N is the total number of inclusions, I_T is the total intensity of the ion, A_T is the total area of the image in μm^2, and A_I is the total area of the inclusions.

Knowing K_s, the number of replicate analyses (N) required for a confidence interval $\Delta(\%)$ where sampling is the major source of error can be calculated as

$$N = (100tK_s/\Delta(\%)a_0^{1/2})^2$$

where a_0 is the area sampled and t is taken from the Student t tables at the desired confidence level. Marinenko and coworkers (*304*) outlined a procedure for testing the microhomogeneity of standard reference materials such as alloys and glasses by electron microprobe measurements.

Van Craen determined the variability of a number of NBS standard reference materials at the microscale level by ion microscopy (*480*). His results are in reasonable agreement with those of Morrison and others.

Sampling of molten metals is required in the metals refining industry for control of the refining process. Helle described the rationale behind the choice of sampling procedures followed at a steel works in Natal (*211*). Newbold presented a historical perspective of sampling steel for carbon, hydrogen, nitrogen, and sulfur (*342*). Ormrod (*352*) tested a sampler-filter to monitor the extraction of gold in the carbon-in-pulp extraction process. Problems in sampling aluminum (*55*), copper (*478*), molybdenum and tungsten (*354*), scrap metals (*19*), and precious metals (*385*) have also been addressed. Protzer (*380*) has described sampling techniques for ingots that can overcome variability from segregation on cooling. Lundell and Hoffmann illustrated the magnitude of variations of C, Si, S, and P that can be expected in a steel ingot (*294*).

Automated analytical methodology for furnace control in the steel industry is requiring a new look at the sampling step because it is becoming the rate-determining process. McCaig and co-workers (*316*) discuss this problem and have developed a paddle and pin shaped (Diskpin) sampler to fill a multipurpose role for several kinds of analytical measurements. Linde (*288*) discusses techniques and procedures for solid sampling of a basic oxygen steel furnace, including the pneumatic transport of hot (2200 °F) lance samples to the laboratory. Numerous other papers and patents describe sampling devices for molten steel, especially in Germany and Japan (*17, 32, 260, 325, 349, 355, 372, 391, 463*).

Szonntagh has described a microdrilling procedure to sample the metal content of archaeological coins (*467*). In this application it was desirable to take representative samples without defacing the coin. Direct analysis of the coin surfaces by nondestructive techniques had been shown to give data which was not representative of the coin composition. The prescribed microdrilling technique samples a cross section of the coin without damaging the faces by penetrating the coin at the cylindrical surface.

Van der Kuur described a press designed to remove 5 mm diameter samples from a nuclear reactor pressure tube for subsequent hydrogen analysis (*484*). The press reduced sampling time and avoided hydrogen contamination.

Watts (*498*) presented sampling plans for determination of the degree of corrosion in splash zones of an ocean pier. In this work, designed to monitor the stability of the structure, the extent of corrosion was measured by caliper.

OIL AND GAS

The sampling of petroleum and petroleum products is addressed in ASTM D4057 (*14*). The methods described may be applicable to many noncorrosive liquid industrial chemicals as well. The sampling of liquified natural gas is discussed by Welker (*502*), who describes a method of collecting a composite sample and maintaining the product as it is in the pipeline from the start of the sampling operation to the final analysis. Measurement of sediment and water in crude oil requires critical definition of the sample. This question is addressed by Graves (*177*) and Hanzevack and co-workers (*198*).

A strategy for surveying oil spills based on classical sampling theory has been developed by Smith (*445*). It uses oversampling in a first round, with measurement restricted to easily measured properties. The second round involves subsampling of the first samples for the more costly chemical and biological analyses. Sampling procedures for monitoring the quality of natural gas have been considered by Williams (*522*), Lloyd (*291*), and Schepers and co-workers (*408*). Curry has proposed a standard sampling system for estimation of the water-vapor content of natural gas (*107*).

Dusseault studied the problem of sample disturbance when taking cores from oil sand deposits (*126, 127*). Historically, core expansion during sampling due to the release of gas dissolved in the oil and water has resulted in overestimation of deposit porosity and permeabilities.

An apparatus and process for homogenizing and subsampling streams such as those present in the hot water extraction process for recovery of bitumen from oil sand are described by Cymbalisty and Shaw (*108*).

WATER

General Considerations. Several national and international standards address water sampling. ASTM D3370 (*11*) considers the entire question of water sampling as does ISO 5667, Parts 1 and 2 (*225*).

Reviews in the *Journal of the Water Pollution Control Federation* (*70–72, 212, 213, 427–430*) provide many references to sampling procedures and problems. The practical problems of sampling different kinds of waters have been considered by Batley (*35*), Kingsford and co-workers (*252*), Ottendorfer (*357*), Wagner (*492*), Josefsson (*246*), and Gudernatsch (*187*). Liebetrau (*285*) has examined sampling schemes suitable for a statistically valid water quality monitoring system. Autocorrelation of weekly and monthly series of analyses for species such as iron, silica, nitrate, and phosphate in Quebec waters to define optimal sampling frequencies has been studied by Bobee and Cluis (*57*). Bobee and co-workers (*58*) also performed a similar study on the Yamaska River basin in Canada. A time and cost effective sampling strategy to detect violations of pollution regulations has been developed by Hiedtke and Armstrong (*209*). Sampling procedures have been outlined for various chemical pollutants by Whitlock and Paulson (*516*), for environmental contaminants by Dennis (*117*), and for trace metals by Mart (*307*), by Meranger and co-workers (*323*), and by Laurent (*277*). Problems in sampling for mercury in natural waters and in precipitation have been discussed by McLean and co-workers (*320*). Owens and co-workers (*358*), on the basis of a study of four methods of sample collection and preservation, concluded that general cleanliness and the type of filtering apparatus had far more effect on the results than did the method of collection. They recommend minimum processing in the field. The sampling and measurement of hydrocarbons in natural waters was considered by De Lappe and co-workers (*114*). Smith and co-workers (*444*) evaluated the literature on sampling and preconcentration methods for the analysis of polycyclic aromatic hydrocarbons in water systems. A double sampling procedure was recommended by Drozd and Novak (*121*) for the assay of trace hydrocarbons in water by quantitative head space gas chromatography.

Jeffries and Zimmerman (*238*) commented on the problem of sampling low conductivity natural waters for alkalinity. Krajca (*262*) described the methods available for the sampling and analysis of natural waters for gases.

Harrison (*205*) has pointed out that the ability of neutron activation analysis to monitor many elements simultaneously in individual samples of differing types makes it a useful tool for the study of water sampling techniques.

Surface Water. A large set of data on water quality in the Great Lakes, which includes sampling times and methodologies, has been studied by Gregor and Ongley (*181*). Sanders (*402*) has presented a criterion for zones of relatively complete mixing in a river which would require only one sampling point to collect water quality data representative of a cross section of the river. Such zones, if present, would be ideal locations for water quality monitoring stations. On the basis of phosphorus analyses of grab samples collected on various time schedules in a New York creek, Johnson (*239*) concluded that acceptable estimates of the yearly solute flux in a stream can probably be obtained from weekly grab samples. Whitfield (*514*) found that only one out of four sampling sites on the Yukon River gave sufficiently representative samples to be useful in water quality evaluation. The general topic of water quality sampling programs in rivers has been considered by Dandy and Moore (*110*). Otson and co-workers (*356*) concluded that sampling and storage conditions had little effect on total organic carbon levels at moderate concentrations, but contamination could be significant at low levels. Beasley (*39*) has compared three sampling methods for nonpoint source pollution in forest streams, while McGuire and co-workers (*319*) have used paired samples to compare sample intake position and loading rates from nonpoint source pollution. Changes in phosphorus inputs into a stream with flow rate were studied by Sharpley and co-workers (*424*). They found varying sampling intervals were necessary, depending on whether surface or subsurface runoff was being evaluated. Fraser and co-workers (*156*) investigated sampling techniques for mineral-rich springs used by wildlife. Conflicting results among previous studies were attributed to inappropriate sampling. A variety of techniques for the sampling of the surface microlayer of natural waters for proteins were assessed by Gucinski and co-workers (*186*). Sampling strategies for stream sediments were evaluated as a function of the goal of the analysis by Bouvier and co-workers (*62*). A survey of a drainage basin in Alaska by Johnson and co-workers (*240*) involving multielement spectrographic analysis of a large number of stream sediment samples for 34 elements showed that about half of the total variation arose from sample preparation and analysis. Statistical analysis of the data indicated that the sampling frequency was sufficient to show that large geochemical anomalies were not present. Whiticar (*515*) has described a method for the "in situ" sampling of ocean sediments for interstitial gases and fluids.

An inexpensive and simple sampler useful for profiling a water column is described by Merks (*324*). Youngbluth and co-workers (*533*) found that a water column sampler gave the same results as a discrete-depth sampler for inorganic nutrients in a shallow lagoon. Phillips (*368*) described a rotating sampling arm useful for the collection of large numbers of samples for such determinations as chemical oxygen demand. An all-Teflon multichannel positive displacement apparatus for collecting composite samples is described by Tigwell and co-workers (*472*).

Stabilization of water samples is discussed by Scheuermann and Hartkamp (*409*) who recommend pretreating surfaces of containers with Al^{3+} ions or by shock freezing of samples at liquid nitrogen temperatures immediately after bottling. Sorption losses have been studied by Massee and co-workers (*309*). Laxen and Harrison (*278*) describe cleaning methods for polyethylene sample containers for trace metals in water. The general subject of on-site sampling with preconcentration for trace metal analysis has been reviewed by Meranger and co-workers (*323*). The use of Sep-PAK cartridges for collection and concentration of low-level constituents has been discussed by Wolkoff and Creed (*528*). Ion exchange resins are evaluated and methods for preparation of resins of special use in pollutant collection are given by Chikuma and co-workers (*96*). Harris and co-workers (*202*) have evaluated macroreticular resins for general and compound-specific sampling of organics in water. They recommend a combination of the two dissimilar resins XAD-2 and XE-347 for collection of both nonpolar and polar organic compounds.

The use of microreactors containing immobilized urease for sampling mercury ions is discussed by Oegren (*351*). A solid extractant made with the liquid anion exchanger Adogen 464 supported on silica gel has been reported by Battistoni and co-workers (*36*) as useful for recovery of anionic metal complexes as well as simple anions. Commercial 10-mL disposable syringes have been used by Matsui (*311*) to prepare samples for oxygen-18 measurements in water samples from river deltas. Analytical gas scrubbers for the quantitative extraction and concentration of volatile or gaseous components of water have been described by Bosset and co-workers (*60a*) and by Grote and Westendorf (*184*). Large-bore coated columns are described and used by Mackay and Hussein (*298*) as sampling and concentration traps for traces of organic volatiles in air and water. High-speed, continuous-flow centrifugation and glass-fiber filtration were used by Bates and co-workers (*34*) to sample suspended matter from river water and wastewater for hydrocarbon analyses. Both methods collected the same range of particles, but the glass fibers adsorbed organic compounds.

Groundwater. Statistical considerations and sampling techniques for the monitoring of groundwater quality have been presented by Nelson and Ward (*340*). Guidelines for sampling of groundwater (*280*) and for monitoring wells (*413*) have been made available. Fetter (*146*) has described sources of error that cause contamination in groundwater samples. Slawson (*438*) has evaluated sampling methods for the analysis of groundwater quality in the oil shale regions of Colorado. Nightingale and Bianchi (*346*) discussed the effect of water quality variability on sampling decisions using the philosophical doctrines of probabilism and relativism, while Wilson and Rouse (*526*) pointed out that sampling of monitoring wells may give results that are not representative of formation water. Procedures for the collection of representative water quality data from monitoring wells have been provided by Gibb and co-workers (*166*); the same topic has been considered by Halfen (*195*) from the point of view of the effect of sludge disposal on the quality of groundwater. Riha (*390*) has stressed the importance of valid multistage sampling in the testing of groundwater for evaluation of aquifer systems. The low velocity of groundwater under nonpumping conditions makes the particulate load negligible. Strausberg (*458*) has noted that samples must be checked for turbidity, which can give rise to erroneously high heavy metal concentrations for such waters.

Representative averages of heavy metal concentrations in groundwater and precipitation from mountain forests could only be obtained by collection of weighted samples over several years, according to Mayer and co-workers (*314*). Bricker (*73*) provided guidelines for sampling and analysis of interstitial waters for dissolved chemical species. Edmunds and co-workers described techniques for sampling deep aquifers from boreholes drilled for geothermal exploration (*133*). Analyses of brines from geothermal wells in the Imperial Valley of California were found by Needham and co-workers (*339*) to be highly dependent upon sampling times and conditions. A study by Betz and co-workers (*50*) of the behavior of several pesticides and chlorinated hydrocarbons in a 100-m long artificial aquifer fed with seepage water from an aerobic land fill was found to be strongly affected by both sampling and measurement problems. Johnson (*243*) has reviewed methods for monitoring cyanide in groundwater near cyanide leach mining sites. The influence of sampling and well construction on the properties of groundwater collected near oil shale deposits has been described by Slawson and co-workers (*439*).

Groundwater sampling utilizes wells which must be carefully sited. Drilling, casing and screening, and maintenance are critical factors affecting the quality of the analytical data. Such problems are discussed in some detail by Halfen (*195*). Shuller and co-workers (*413*) discuss the matter further with special considerations of flushing and other operational details that are important to ensure representative samples. Methodology for drilling wells for groundwater analysis utilizing hollow stem augers is discussed by Everett (*140*). Pettyjohn and co-workers (*367*) describe a variety of sampling equipment developed at the Robert S. Kerr Environmental Research Center for organic contaminants of groundwater. Harrar and Raber (*201*) describe an apparatus designed to collect groundwater samples in locations of limited water flow when atmospheric contamination must be avoided. Barbarick and co-workers (*33*) compare various methods of sampling soil water for its ionic salt content.

Seawater. The book "Methods of Sea Water Analysis" (*175*) includes sections on sampling and sample handling of ocean waters. A practical guide to measurement methodology by Carlberg (*86*) emphasized marine chemistry. Green (*179*) has critically reviewed methods of sampling water depth profiles and surface films for hydrocarbon determinations and has provided a set of recommended procedures. Variations in the levels of volatile organic compounds in the air and water at a coastal site were followed over several seasons by Mantoura and co-workers (*303*); they found that sufficiently high sampling frequencies revealed summer weekend and winter week effects. Ahmed and co-workers (*15*) found that sampling variability was the largest source of uncertainty in the determination of petroleum in Boston Harbor. The effects of different sampling techniques in the determination of suspended metals in coastal waters were discussed by Duinker and co-workers (*122*), and Simpson (*434*) reviewed sampling methods, along with effects of particle size and concentration, on the measurement of particulate matter in the oceans. The theory of particle dynamics is finding many practical applications in such systems.

Erickson (*138*) has reviewed the techniques, apparatus, and materials needed to sample and store seawater for trace metal analysis and has provided recommendations on sampling and storage procedures. Means of reducing contamination effects by proper choice of cleaning and handling techniques are discussed and recommended sampling and storage methods are presented. Massee and co-workers (*309*) also surveyed sorption of many elements from aqueous solution, and measured losses of several metals from artificial seawater during storage in glass, polyethylene, and Teflon. An all-Teflon sampler that avoids any contamination of deep water samples by the sampling equipment has been developed by Harrison and co-workers (*206*). Spencer and co-workers (*451*) found Teflon bottles to be superior to Teflon-coated GO-FLO samplers for lead and zinc. Bewers and Windom (*51*) compared three types of sampling devices for trace metal determinations and concluded that modified GO-FLO samplers gave the least contamination, followed by modified Niskin samplers. Unmodified GO-FLO and Hydro-Bios samplers gave similar, but poorer, results. Of the wires used to suspend the samplers, plastic-coated steel gave negligible, and Kevlar and stainless steel only slight, contamination for some metals. Sturgeon and co-workers (*461*) used silica-immobilized 8-hydroxyquinoline to preconcentrate eight metals prior to determination by graphite furnace atomic absorption. The procedure of use of small boats provided with sample bottles attached to a telescopic bar is recommended by Mart (*307*) as a means to minimize contamination from the research vessel in coastal water sampling. A towed system for continuous profiling of chemical parameters in the sea at depths ranging from 3 to 100 m is described by Grasshoff and Hansen (*176*). An apparatus for taking samples of water at a depth of less than a millimeter has been described by Prati and Disaro (*376*), who claim that the samples obtained are independent of the hydrodynamic characteristics of the waters under study. Van Vleet and Williams (*483*) have compared 14 techniques for sampling the sea surface monolayer with respect to collection efficiencies. Filters were found to yield the more representative samples. A bubble-adsorption technique to produce aerosols enriched with surface-active organic matter has been described by Gershey (*165*). A device for sampling at the sea bottom, consisting of a Nansen bottle with suitably activated closure, has been developed by Sipos and co-workers (*436*). Methodology has been described by Pavlou and co-workers (*362*) which permits collection of seawater samples for chlorinated hydrocarbon residue analysis, avoiding contamination by surface films. Sampling of seawater for dissolved gases is always plagued with possible loss of gases from the collected samples. Cline and co-workers (*97*) have designed a simple syringe sampler that is said to avoid the problem. Worthington (*530*) recommends encasement of the Nansen bottle collector with thermal insulation to minimize degassing from warming of the samples when they reach the surface.

The use of the brown seaweed *Ascophyllum nodosum* as a marine monitor for trace metals has been considered by Woolston and co-workers (*529*).

Industrial Water and Wastewater. The practical aspects of sampling rivers, industrial effluents, and sewage have been considered by Schofield (*410*), Shelley (*425*), and the Research and Education Association (*453*). A team of chemists from the German Chemists Association has tested simple methods for the preservation of samples of municipal effluent (*164*). Sampling and analytical studies of influent, effluent, and sludge from several publicly owned water treatment works were carried out by Carr and co-workers (*88*). Tests were made for 13 heavy metals and 115 synthetic organic compounds. Fisher and Claeys (*148*) have discussed factors important in the organization of sampling and measurement programs for priority pollutants in wastewater. They stress the importance of precautions in the procedures specified for sample collection and preservation and in the use of appropriate sample containers. The problems associated with representative sampling of oily water effluents for oil content have been outlined by Palmer (*359*).

A number of studies have reported on the sampling and measurement problems associated with radioactive wastes. Romero and co-workers (*395*), in an investigation of the transport of radioactivity from a solar evaporation pond to the soil, air, and vegetation around it, described several sampling procedures. The use of ion-exchange resins to sample solutions of spent reactor fuels has been discussed in a general way by Smith and co-workers (*442*). Goergen (*170*) has described the removal of samples from high-level radioactive waste tank supernatant solutions at the Savannah River Plant in South Carolina. Illy (*227*) has assembled a bibliography on sampling and measurement problems of primary coolant in pressurized water reactors, while Moffett and Zoski (*330*) and Brown and Massey (*77*) have discussed the problems of sampling for corrosion products in conventional high-pressure boilers. The related problem of sampling boiler steam condensates for corrosion-inhibiting amines has been treated by Malaiyandi and co-workers (*301*). Leslie and Moore (*284*) found that an investigation into the physical effects of entrainment on suspended particulate matter in condenser cooling water from electric power generating stations was frustrated by an impotent sampling program; this frustration was revealed in the last phrase of the title: "An Exercise in Futility".

Other waste sampling problems that have been addressed include effluents from meat packing plants (*102*) and sewage plant sludges in Indiana (*449*). Mitchell and co-workers (*329*) found that samples of sewage sludge could not be reliably homogenized for mercury analysis by manual mixing but could be by a commercial mortar mixer.

Precipitation. The measurement of atmospheric deposition, both wet and dry, is a subject of considerable current interest and one in which the data are highly dependent on the sample and sampling process. Granat (*174*) has identified the important principles to be considered in the design of a network to measure precipitation in a region. Among the factors discussed are averaging times (event, month, year) and the use of temporary additional collectors as a tool in the overall network. Estimates are given of the probable error to be expected in average precipitation values as a function of the size of the area under study and the number of sampling stations. An analysis by Baker and co-workers (*31*) of measurements of sulfur in rain made as part of a multistate pollution study indicated inadequacies existed in the collecting and reporting procedures. Recommendations for future rain chemistry programs were made. Rainfall acidity and ionic composition were investigated in the vicinity of the Kennedy Space Center by Madsen (*299*), who found that concentrations from five sites within a 200 km^2 area agreed well with values collected from 13 sites within a 600 km^2 area. The effects of sample collection schedules on results of nutrient measurements in rainfall and throughfall in forests were assessed by Peterson and co-workers (*366*). Snow has been the subject of studies by Stengle and co-workers (*456*), who sampled glacial snow on Mt. Logan for pesticides. Peel (*363*) investigated organo chlorine residues, and Bowtron (*64*) trace elements, in Antarctic snow.

Samplers have been described which measure both wet and dry deposition, for example, dust-fall buckets (*10*), and exclusively one or the other. Volchok and Graveson (*491*) describe collectors fitted with covers activated by precipitation sensing devices, and that have heated sensors that can respond to frozen precipitation. Aichinger (*16*) describes a fully automatic monitor to collect both wet and frozen precipitation. Sequential sampling has become of recent interest in recognition of differences in composition of wet deposition during the course of a storm. Robertson and co-workers (*394*) discuss various techniques, including manually segmented samples, linked collection vessels, automatically segmented samples, and continuous monitors. They give a detailed description of the so-called West Point Sampler developed by this group. Raynor and McNeil (*384*) have developed an automatic sequential precipitation sampler which collects both wet and frozen, but excludes dry, precipitation. The problem of deterioration of samples as related to storage time and interaction with containers is discussed by Samant and Vaidya (*400*).

Miscellaneous Water. The importance of adsorption of insecticide residues on environmental sampling and measurements was pointed out by Miles (*326*) in a study of the contribution of insecticide-contaminated farm soils to nearby marsh water sand sediments. Smith (*440*) has discussed in a general way strategies for the collection and concentration of drinking water samples for the determination of organic contaminants. LeBel and Williams (*279*) found sampling to be a major source of error in an investigation of tributoxyethyl phosphate levels in tap water. Sampling theory has also been used by Short (*426*) in the design of a program to assess water quality during distribution and by Hanke and Mehrez (*197*) in the setup of a system to collect data for optimization of predictions on water use. The need for adequate sampling to identify a pollution source in Lake Mead was clearly illustrated by Everett and co-workers (*141*).

SEDIMENTS

An ASTM standard practice ASTM D3977 (*13*) describes sampling procedures for the determination of suspended sediment in water samples. Another standard, D3976 (*12*), describes procedures for use in homogenizing such samples and for drying prior to analysis.

Accurate description of marine sediments is complicated not only by the physical problems involved in obtaining a sample but also by the dynamics of the environment. A study of the particle size distribution of sediments in the Tay Estuary showed that the distribution was dictated by the natural tendencies of different size fractions to accumulate preferentially in various regions of the delta, by significant changes which occur over time within a specified sampling zone due to channel and tidal flow, and by the fact that up to four subpopulations of grains may be present (*321*).

Walton has prepared a report describing the sampling and analytical plans required to monitor the environment for inforcement of the Canadian Ocean Dumping Control Act and the International Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter (*495*). The report describes in detail various types of samples, methods of sample storage, and documentation.

Variability in the concentration of weak acid leachable metals in ocean sediments has been used to determine sampling plans which will detect future changes in concentration (*371*). Garrett and Goss evaluated sampling and analytical variations in surveys of lake bottom sediments. Less than 3% of the total variance was attributed to analytical variability plus variability within lakes (*162*). However, analytical replication was still recommended to monitor subcontractor performance.

Avilov and Trotsyuk (*28*) have developed equipment that permits the hermetic sampling of bottom deposits and their vacuum degassing on board ship for gasometry operations. The process is said to minimize gas loss that would otherwise occur. A close-interval in situ sediment pore water sampler has been developed by Montgomery and co-workers (*332*). It can sample at 1-cm intervals without disturbing the sediment. Vertical profiles for ammonium, reactive phosphate, nitrate, nitrite, and silicate in pore water can be obtained in an anaerobic environment. Summerfield (*464*) has devised a probe for chemical and gas analysis of mire waters. Filtration and centrifugation techniques for separation of suspended particulates in coastal water have been compared by Duinker and co-workers (*122*). Samples of mineral flocs drawn from Niskin-bottle samplers were found by Gibbs and Konwar (*167*) to not be representative of the floc sizes in the bottle.

Hoepner (*218*) describes the design and use of a diffusion sampler with 20 chambers located over a distance of 33 cm for the examination of interstitial water in fine grained sediments. This is also the subject of a paper by Hertkorn-Obst and co-workers (*214*). Sampling for the analysis of interstitial gases and fluids in sediments was discussed by Whiticar (*515*). The use of ping pong balls and latex tubing for extracting helium from lake sediments, and thereby detecting fault and fracture zones, was discussed by Dyck and Da Silva (*128*).

ATMOSPHERE

Gases. Most sampling of the atmosphere is conducted with the ultimate goal of measuring pollutants or their effects in either a localized setting for industrial hygiene or monitoring on a more global scale for environmental studies. Two exceptions were papers describing the sampling and measurement of boron (*150*) and dinitrogen oxide in air (*337*); these studies were conducted to identify the geochemical cycle of both species in the atmosphere.

Lodge (*292*) has considered the problem of ensuring representative samples of atmospheres. Biennial reviews on air pollution (*154*) include some references to sampling. Reviews describing sampling of the atmosphere in general (*79*) and in industrial (*335*) and urban (*273*) settings have been prepared. The book "Methods of Air Sampling and Analysis" includes a collection of 136 methods for the sampling and analysis of ambient and workplace air for various gaseous and particulate materials (*249*). Most of the methods have also appeared in the American Public Health Association journal *Health Laboratory Science*. Another book, "Fine Particles in Gaseous Media" describes the principles of particulate movement in gases as well as particle collection principles and techniques (*215*). A book on aerosols (*289*) includes sampling of these components in the atmosphere. A chapter on sampling and calibration of gaseous pollutants by Axelrod and Lodge (*30*) provides a broad but useful treatment.

General considerations for obtaining samples of gaseous compounds in other gases and especially air were reviewed by Bicking (*53*). Sampling methods for pesticides in air were discussed by van Dyk and Visweswariah (*481*). Traditionally these have involved entrapment in a reagent solution or direct analysis by a suitable instrument. Their review included a general discussion of experimental designs, sampling rates, sample sizes and techniques for sampling pesticides in aerosols once vapor forms. Miller and co-workers described a technique for sampling residual propoxur in air in the vicinity of application of the insecticide (*327*). In their procedure air was drawn through an impinger charged with NaOH trapping solution. Air sampling times greater than 60 min were shown to cause significant losses of the trapping solution and insecticide. Seiber and Woodrow evaluated the concentration of airborne residues of paraquat downwind from a spraying of cotton fields and the exposure to workers during subsequent harvesting for the purpose of recommending occupational practices (*418*). Sampling designs and techniques are discussed throughout their paper.

The carcinogenicity of certain polycyclic aromatic hydrocarbons (PAH's) has made their measurement in the air important at trace levels. Butler, Crossley, and Colwill verified that PAH levels in air are a function not only of the amount of PAH generated but of the meteorological conditions, whereas total suspended particulates are not so greatly affected by weather conditions (*81*). They concluded that PAH's are associated with submicrometer size particles whose dispersion is greatly affected by prevailing conditions. Tomingas reported that filter collection of PAH's can result in significant underestimation of atmospheric levels and recommended special sampling procedures to reduce the loss of PAH during sampling and storage prior to analysis (*474*). Other workers have correlated sulfate particulates produced from SO_2 emissions from fossil fuel generating plants and automobiles to visibility range (*287*) and to health problems such as eye and throat irritations (*535*). Although only indirectly related to sampling, descriptions of the treatment of the data in both papers are useful. Methods for sampling sulfur dioxide (*29, 152, 224, 241, 503*) and nitrogen dioxide (*82, 105*) have been described. Husar and co-workers provided a good discussion of the sampling designs and equipment required when sampling for sulfur dioxide and sulfate particulates from an aircraft (*224*).

A statistical evaluation of a total ozone sampling network has been reported by Moxim (*336*). In two separate papers Sevirs and co-workers have concluded that in sampling turbulent atmospheres for ozone, sampling periods of 10 min or greater are required to produce representative data (*422, 423*).

Pellizzari and associates described the performance of a Tenax GC cartridge sampler for sampling trace organic vapor pollutants in ambient atmospheres (*364*). The paper contains some 20 references to other studies on sorbents for trapping a variety of air pollutants and includes a useful study of breakthrough for several sorbents, along with effects of humidity, background pollution, sorbent reuse, and storage of collected samples.

A large body of literature on sampling gases in industrial settings is available. Stack sampling for odor and total hydrocarbons was addressed by Schuetzle (*411*). Tedlar bags were found to be more suitable than polyethylene, Saran, or Mylar bags, but compared to on-site measurements losses from Tedlar bags ranged from 7 to 38%. Sampling from incinerator stacks (*95*) and laboratory exhaust stacks (*488*) has been briefly described. Trozzo and Turnage (*477*) described a roof monitor sampling technique which utilizes battery-powered personal samplers and a portable velocity meter. The system is applicable to low particulate concentrations and low exit velocity. Bauman has developed a model allowing location of sampling points in a stack that are representative of equal volume rather than equal areas (*38*). Sidor described a colorimetric method for measuring halogenated hydrocarbons in air (*432*). However, the method does not permit differentiation between compounds of the same halide.

Auf der Maur and Lauffenberger described a simple technique for sampling HTO from the air in a luminous paint plant (*27*). A capped soft plastic bottle was taken to the sampling point, the cap removed, the bottle squeezed several times to replace resident air with air from the environment, and the cap replaced. When the bottle arrived at the laboratory, water was quickly poured into the bottle, the contents were shaken to equilibrate the H_2O and HTO, and the HTO was measured by liquid scintillation. The Vacu-sampler (*328*), with suitable modifications for introducing water, would seem to us to provide better accuracy and control. Sampling and analytical techniques for the determination of acrylic acid (*487*), vinyl chloride (*276*), vinyl acetate (*149*), and toluene diisocyanate (*41*) are available.

Novel approaches have recently been developed based on solid-state collection. Axelrod and Hansen (*29*) discussed the use of impregnated filters for collecting SO_2. Forest and Newman (*152*) extended this idea utilizing the high volume sampler. An airborne system described by Johnson and Atkins (*241*) uses the same collection principle. Solid sorbents for atmospheric sampling have been discussed by Greifer and co-workers (*182*). The use of Chromosorb has been discussed by Foerst and Teass (*149*) and silica gel, by Vincent and Guiant (*487*). Problems in the use of activated charcoal were described by Fraser and Pearman (*157*). Posner and Okenfuss studied the desorption of organic analytes from activated carbon by using carbon disulfide as solvent (*375*). They concluded that desorption efficiency for a polar compound was increased if other polar compounds were present.

The familiar gas detector tubes are actually collector–analyzers. Their use in analysis of volcanic gases was described by Piccardi (*369*) (whose concern for reducing sampling times is understandable) and in the determination of toluene diisocyanate by Belisle (*41*). The important question of adsorption breakthrough is discussed by Grubner and Burgess (*185*). The old technique of collection of gases in preevacuated cylinders was considered by Miller and co-workers (*328*). Gas sampling bags of Teflon are recommended for ultraclean or corrosive applications. They are available from various manufacturers with either Teflon-faced septums for sample introduction and removal by hypodermic needle or with nickel-plated on–off valves and tubing connections. Sampling bags of poly(vinyl fluoride) (Tedlar) are less costly than Teflon but are not recommended for corrosive gases. They can be used with CO, SO_2, H_2S, and mercaptans. Sampling by reverse permeation was treated by West and Killick (*503*). Cryogenic sampling, another well-tested technique, was found to be very effective for stratospheric sampling by Ehhalt (*135*). A closed-loop sampling system which returns the sample to the area from which it was taken is the subject of a recent patent (*58a*).

Watada and Massie described an automatic sampler–analyzer for continuously recording the evolution of CO_2 and ethylene by harvested horticultural crops (*497*). Leesch described detector tubes that measure atmospheric phosphine in the vicinity of stored agriculture products (*282*). Morris and co-workers determined the concentration of ethylene dibromide in the air and in ripened fruit (*334*).

Personal Monitors as Atmospheric Samplers. Personal monitors have been the subject of considerable interest in recent years because they strive to estimate human exposure. They may be classified as "active" or "passive", depending on whether a pump is or is not included in the system. Wallace and Ott (*494a*) have published a comprehensive review of the subject with special emphasis on criteria pollutant monitoring. The fundamental principles of passive vapor sampling have been reviewed by Fowler (*153*) who also discusses the comparative merits of diffusion and permeation samplers. Rose and Perkins (*396*) reviewed the state-of-the-art of passive dosimetry with special emphasis on monitoring in the workplace atmosphere. Their discussion of measurement error is particularly good. Cadoff and Hodgeson (*82*) discussed the construction and operational characteristics of passive samplers for exposure to pollutants at ambient atmospheric levels with short-term sampling periods of 1 h or less. Passive dosimeters for solvent vapors using conventional gas detector tubes were described by Hill and Fraser (*216*). Samimi and Falbo have studied the efficiency of Abcor organic vapor dosimeters under various air velocity conditions and exposure to various concentrations of styrene, ethyl acrylate, and *n*-butyl acrylate. They found that the dosimeter sampling constants were significantly affected by air velocity but not by concentration within the critical loading limits (*401*). Turner and co-workers (*479*) have designed a personal monitoring system for respirable particulates (RSP) which has been used in several health-effect studies. Bright and Fletcher (*74*) have developed an RSP monitor that can collect two size fractions—"fine" (less than 2.5 μm) and "coarse" (2.5 to 10 μm). Separate sampling heads can be attached to allow an upper cutoff of 7, 10, or 15 μm. A portable monitor, capable of determining mass but not chemical composition, has been designed by Sem and Homma (*420*) which employs the piezoelectric principle of measurement.

Particulates. Particulates in the atmosphere are a health concern. Sampling of them is complicated by differences of opinion as to what should be collected. The analytical information desired by health agencies is changing from total to respirable and even inhalable particulates, so samplers need to be developed with the model in mind. An ASTM method for sampling stacks for particulates is available (*7*). Carvagnaro (*90*) has compiled a bibliography of over 200 references, with abstracts, on sampling particles in the atmosphere. Gordon and co-workers discussed the level of sampling and analytical effort required for the success of receptor models used to predict the ambient level of atmospheric particulates (*171*).

In their paper describing particle size distribution of urban lead aerosols, Roberson and Ludwig described in detail field sampling techniques and criteria for site selection (*293*). Lynam determined that lead from automobile exhaust is deposited rapidly (*296*). Approximately 50% of the lead settles within 200 m of the source.

Filtration is a long-standing sampling technique. Pierce and Meyer concluded that analysis of segments of filters used to collect lead aerosols is markedly inferior to analyzing the total filter (*370*). Seeley and Skogerboe presented a novel approach for filtration whereby graphite electrodes from an atomic emission spectrograph were also used as filters for collecting the sample (*417*). Malanchuk (*302*) discussed the relation of filter materials to the gravimetric measurements of collected particulates. Filter materials of high purity have been developed by Benson and co-workers (*45*); composed of 99.2% SiO_2, these microquartz filters can collect at temperatures of 500 °C, are insensitive to humidity, and are insoluble in most acids. Five types of membrane filters were studied by Mark (*305*), who describes certain measurement problems associated with them. Lundgren (*295*) describes a four-stage impactor for classification of particle sizes and includes a calibration procedure.

Cascade impactors are reviewed by Van Grieken and co-workers (*482*) and especially in the case of their use with proton-induced X-ray emission (PIXE) analysis. A small centrifuge for source sampling has been designed and constructed by Anderson (*23*). It is thermally protected and small enough for use in-stack. The problems of sampling airborne particles are illustrated in a paper by Johnson (*242*) on characterization of stack and automotive emissions. Sampling techniques have also been described for the characterization of roadway dust (*219*) and particulate matter emitted by coal-fired boilers (*318*).

BIOLOGY

Biological sampling may have several different connotations depending upon the interests of the reader. For the biologists who for unknown reasons may be reading this review, sampling may imply the collection or counting of species in an environment. For the chemist, the first thought is probably the sampling of biological tissues for subsequent chemical analysis. In some applications, metals in fish for example, proper samplings of the biological population in the environment and the tissues in the laboratory are required (*145*). For this reason, some discussion of both aspects of biological sampling is included.

Green's book "Sampling Design and Statistical Methods for Environmental Biologists" covers aspects of experimental planning and data manipulation (*180*) that may be useful reading as a general reference for chemists. Equipment and field sampling methods are not treated. The book "Sampling Biological Populations" (*103*) is also helpful in this area. Eberhardt and co-workers (*131*) have provided models for sampling for contaminants in ecological systems in general.

A self-propelled sampler for collecting wireworms in soil was described by Smith and co-workers (*441*). Factors associated with accuracy in sampling fish eggs and larvae have been discussed by Bowles and co-workers (*63*). The study emphasizes apparatus and procedures. Atsatt and Seapy conducted a statistical analysis of data collected from midwater trawls in the Pacific to compare biomass numbers and mean sizes of fish and crustaceans (*25*). They decided that ten trawls are required to predict a population mean in that environment. Landin compared methods for collecting water beetles (*275*). Saila and associates discussed sampling of invertebrates from the New York Bight in terms of number of samples required to obtain the desired precision and to determine the most cost efficient sampling plan (*399*). Sell and Evans evaluated a Folsom splitter for subsampling plankton (*419*). Slack and co-workers prepared a useful reference book describing methods of collecting and analyzing aquatic biological samples (*437*). Their approach applies statistical principles to determine the most appropriate sampling strategy. Zarnovican determined that an 8-m grid was sufficient to detect the microheterogeneous structure of vegetation in a bog (*537*). Other papers describe sampling of various species in vegetation communities (*313, 450, 524*). Bernstein and Zalinski reviewed methods that provide a simple model for detecting a significant change in an environment and a power test procedure to determine the degree of replication required to detect a change of predicted magnitude (*46*). They emphasized that biological significance and statistical significance are not necessarily equivalent. The same caution should be exercised when interpreting chemical information. Sampling procedures for protozoa in water (*223, 398*), bacterial colonies on plates (*254, 473*), organisms from fish stomachs (*286*), and microphages in the peritoneal cavity of a rat (*315*) have been statistically evaluated.

Sansoni and Iyengar's discussion of sampling and storage of biological materials for trace elements is of great interest because it contains data describing potential contamination from laboratory environment, reagents, and glassware (*404*). Their more recent review provides a complete compilation of sampling, storage, and sample preparation techniques (*405*) and contains the data from their earlier reference. Moody addressed similar concerns (*333*). Sampling of bone for fluoride content (*465*) and radiocarbon dating (*469*) have been described. Klaas and co-workers studied the variability of egg shell thickness in five species of birds to design optimum sampling schemes that would monitor the effects of DDT and other pesticides on the populations (*255*).

Nichols and Hageman (*344*) described a simple cryogenic brittle fracture technique for pulverizing biological samples after first freezing in liquid nitrogen. Zeisler and co-workers (*538*) developed a cryogenic disk mill constructed of PTFE Teflon which produces an uncontaminated finely ground sample.

AGRICULTURE AND FOOD

Agricultural studies include soil sampling for nutrition, sampling of plants or parts of plants to measure components of interest, often metals, and sampling of the water or air near crops. Some workers have attempted to relate the content of a chemical constituent in vegetation to its content in the soil. Hall and Miller completed an extensive greenhouse study on the effect of phosphorus, season, and sampling method on the foliar concentrations of 16 metals in grass (*196*). They concluded among other things that the availability of phosphorus influenced foliar metal concentrations. Significant seasonal variations occur in the metal content of grass; physiologically young tissue should not be sampled. Wear and Cope suggested that soil sampling is a satisfactory method for determining the needs of a pecan orchard for several elements including Zn, Ca, Mg, and P (*499*). They found poor correlation between soil and tissue values for nitrogen, indicating sampling of leaves is required. Temple and Wills reviewed sampling and analysis of soils and plants (*470*). Price briefly described a system of soil and plant analysis that defines the nutrient needs of crops (*379*).

Numerous researchers have written about sampling of plants for metal content. The topics discussed include both how to select appropriate leaves from a plant and variations within a single leaf. In the former category are discussions of sampling banana trees (*59*), ber trees (*93, 94*), arecanut palms (*531*), lime trees (*234*), clementine (*251*), chiku trees (*360*), mango trees (*91*), kalanchoe (*341*), grass (*113, 454*), coniferous trees (*139*), and poplar trees (*159, 161*).

Researchers have identified variations in metal content among different parts of banana (*271*), grape (*49*), corn (*245*), and sugar cane (*160*) leaves. Metal contents of leaves and wood of peach (*281*) and of coniferous and deciduous trees (*85*) have been determined. Of these articles, that of Cannon, Papp, and Anderson (*85*) illustrates best the variations in metal content to be expected for a variety of trees and plants.

Weis and co-workers identified an uneven distribution of calcium in apples and recommended sampling procedures that would permit determination of the effect of foliar calcium sprays on the calcium content of the fruit (*501*). Bretzloff and McMenamin recommended that paired, opposite sectors each comprising $^1/_{16}$ of a potato provided the most representative sample for magnesium, calcium, and potassium determinations (*69*). They found that coring was unsuitable. Dyson reached the same conclusion in a study of the sampling of swede roots for dry matter and mineral content (*130*). Nilsson analyzed the variation of red and yellow pigments in beetroots and recommended cost efficient sampling schemes for the determination of average pigment content (*348*). Kershaw and Hardwick identified the variability of oil, free fatty acids, and moisture in commercial shipments of shea nuts (*250*).

Horwitz and co-workers prepared introductions to sampling and sample handling in the areas of food safety (additives and contaminants), food composition (nutrient labeling), and food quality (*221, 222*). Lento (*283*) and Roberts (*392*) discussed sampling and statistics relating to the nutritional labeling of foods. Shutze and Benoff identified a wide range in nutrient levels in commercial animal feedstuffs and estimated the number of samples required to obtain reliable nutrient content information (*431*).

Suddendorf and associates proposed a procedure that significantly reduces the sampling variability when measuring lead concentration in canned foods (*462*). Freeman and Horne found that total mercury is uniformly distributed in the edible muscle of swordfish, which simplifies the procedure required to obtain a representative sample (*158*). Gustafsson analyzed 258 samples of fruit, vegetables and roots for carbendazim in combinations of two samples. When the pesticide residue exceeded 0.20 mg/kg in the composite, the parent samples were then analyzed separately. By this sampling procedure a 42% saving in the number of analyses was realized (*188*).

D'aoust and co-workers proved that the whole carcass rinse method is superior to the thaw water and skin methods for detection of Salmonella in poultry carcasses (*109*). Auclair and associates (*26*) and Marshall (*306*) described procedures used to sample milk products for bacteriological analysis. McCaughey and Gordon concluded that dairy cows may be sampled from any quarter for progesterone estimation without significantly affecting the accuracy of the estimate (*317*). Scott and Glass described a sampling device used to take samples for milk fat analysis from bulk tanks (*416*). Reuter discussed the problem of carry over in automatic milk samplers (*388*). This problem is similar to that encountered in autoanalyzers where a sample can be contaminated in-line by the sample which immediately precedes it. Nilson and associates evaluated disposable milk sampling containers for their resistance to leakage during sampling and sample preparation operations (*347*). Williams and Peterson statistically examined composite and milk sampling programs for determination of milk fat, protein, and lactose content (*520*). They calculated that random sampling of fresh milk is cheaper and more accurate than 2-week composite sampling.

Sampling and analysis of foodstuffs for aflatoxins, highly toxic and carcinogenic products of mold growth, are described extensively in the literature. Schuller and co-workers have reviewed aflatoxin methodology in detail (*412*), while DiProssine and Campbell (*84*) have described sampling for aflatoxins in more general terms. Knutti and Schlatter showed that estimates of aflatoxin content tend to be low when only small samples (less than 10 000 kernels) are analyzed (*259*). Berry and Day (*47*) evaluated results of sampling for aflatoxins in diets where most samples contain an undetectable amount. Whitaker, Dickens, and research associates have conducted extensive research in the sampling and analysis for aflatoxins in corn (*510*), cottonseed (*486, 507, 512*), and peanuts. Their work with peanuts provided a series of elegant theoretical investigations of a difficult sampling problem (*382, 505, 509, 511, 513*). It also included development of a sampling mill (*119*), analytical methodology (*506*), and an evaluation of the aflatoxin control program (*118, 508*). Whitaker has reviewed the most important features of these papers (*504*).

CLINICAL AND MEDICAL

Sampling for clinical studies, often addressed in the journals *Clinica Chimica Acta* and *Clinical Chemistry*, will be considered only briefly. Typical problems in clinical chemistry include the sampling of livers by biopsy to determine trace metals as an indicator of haemochromatosis or primary bilary cirrhosis (*350*) and sampling urine in physiological, toxicological, epidemiological, and nutritional studies (*68*).

Errors in sampling and sample preparation for measurement of trace elements in tissues and body fluids have been surveyed by Behne (*40*). Ibbott (*226*) has listed the general requirements for collection of a valid physiological sample. Stanley and Sanders (*455*) have developed a system for sampling signals from heart rate and blood pressure monitoring devices. Spucke and co-workers (*452*) have discussed the sampling and storage of clinical materials, using blood collection as an example. The problems of sampling blood for lead (*67*), various drugs (*60*), serum creatine kinase (*78*), and tetrahydrocannabinol (*83*) have been addressed. Rubin and Forster (*397*) have considered the number and time of collection of blood samples required to define the level of prolactin present following administration of haloperidol. Sampling errors in the determination of calcium and oxalate (*217*) and of sodium (*290*) in urine have been treated. Statistical power analysis has been used by Poland and co-workers (*373*) to determine the appropriate sample size for the study of various hormones in rat serum. Juswigg and co-workers (*247*) studied the effect of a tourniquet on trace metal concentrations in plasma by drawing paired samples simultaneously, one from the free left arm and the other from the ligated right arm of 14 volunteers. A statistical study showed significant increases in zinc and iron concentrations upon ligation; copper levels were not affected. In a similar study McNair and co-workers (*322*) found increases in serum proteins, calcium, and magnesium. Standardization of sampling techniques is clearly important for such measurements.

MISCELLANEOUS

A book by Zief and Mitchell (*539*) on control of contamination in analyses for trace elements includes a discussion of sample collection. Procedures for sampling of hazardous wastes have been provided by Williams and co-workers (*521*). A system for determining the degree of hazard of drums of unidentified waste has been developed by Block and Kalinowski (*56*). An overview of current requirements and techniques for sampling and monitoring radioactivity in the environment of nuclear facilities has been given by Cline (*98*).

The relevance of sample increment size and number of increments to statistical prediction of the likelihood of heterogeneity being present in a blending tank containing polyolefin pellets, even though sample analysis indicates a mixed condition, has been treated by Vance (*485*). Egermann (*134*) has discussed the problem of assessing uniformity in mixtures of powdered drugs at low dosage levels. Sieving of drug–diluent premixes was found to be effective in excluding problems of agglomeration. Rericha and co-workers (*387*), in a study of H_2PtCl_6 catalyst on styrene–divinylbenzene beads, found that the distribution curve for the metal is asymmetric and fits a three-parameter log normal curve. The correlation coefficient between the weight of a single bead and its absolute metal content was 0.56. On the basis of these results a sampling procedure was developed that reduced the sampling uncertainty.

The importance of proper sampling of processing and plating solutions for good analytical results has been discussed by Mohler (*331*). Standardization of the sampling of fertilizers has lagged behind the analytical methodology according to Lance (*274*), who describes efforts to improve sampling practices. The question of extent of contamination during sampling for elemental analysis of hard-fired ceramics by drilling has been addressed by Carriveau (*89*), who found diamond burrs best for materials of high hardness.

The withdrawal in flow injection analysis of a small sample of dispersed zone followed by injection into another carrier stream was considered by Reis and co-workers (*386*). The method was found useful for the automatic dilution of plant tissue digests being analyzed for potassium. In a later paper the same group (*534*) used the method in the simultaneous determination of aluminum and iron in plant material.

Sampling of spent reactor fuels, which is vital to nuclear safeguard programs, is difficult owing to the high radioactivity levels that may be involved. Smith and co-workers (*442*) review the problem and describe a new sample loading technique that involves the use of anion resin beads. This microsampling technique is advantageous because of the small quantity involved, the separation possibilities provided, and the convenience of loading single beads on a filament for mass spectrometric analysis.

A system for sampling effluents from a slagging fixed-bed coal gasification pilot plant is described by Paulson and co-workers (*361*).

A simple and reliable method for taking samples of slurry from settled farm slurry stores by means of a tube and piston sampling device is described by Martzopoulos and Nielson (*308*).

The use of insects for sampling xylem sap, discussed by Newby (*343*), is a novel technique (to the present authors, at least). Aphids feed on the phloem and fluid is collected from the cut ends of the stylets; alternatively the honey-dew can be collected. The article discusses other insects that have been used in a similar manner.

A sampling probe system to study the rate of formation and evolution of polycyclic aromatic hydrocarbons in flames has been proposed by De Lorenzo and co-workers (*115*). Wilks (*518*) has suggested a new sampling method that allows reflectance IR to be used for continuous monitoring of moving streams.

Sampling rates of a photocell traversing over a field of corn to measure mean irradiance levels were studied by Sinclair and co-workers (*435*). A frequency of 4 to 8 s was found satisfactory.

CONCLUSIONS

The problem of obtaining representative test samples from a population has become more evident in recent years as analytical techniques become more precise and as limits of detection become lower. Strategies must be developed to reduce errors of the sampling operations commensurate with the increased sensitivity, precision, and accuracy of measurement operations. Analytical chemists must pay more attention to the overall analytical process, and particularly to sampling, a likely major source of error. To quote from a textbook written over 40 years ago "...the old axiom that a chain is no stronger than its weakest link applies without reservation to the series of operations involved in an analysis. ...time and thought should be expended on the sampling operation, and when the problem at hand is not worth such an effort, neither is the analysis warranted" (*519*).

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APPENDIX B

Determination of Bitumen, Water and Solids in Oil Sand by the Modified Dean Stark Method

Background

The method used to determine the bitumen, solids and water content was adapted from the analytical methods described in Chapter 2, by the Alberta Committee on Oil Sands Analysis (ACOSA)[a], a committee of analysts in the oil sands industry. The accuracy of the method was established by consensus after a series of collaborative studies on the analysis of homogenized samples of oil sand. No standard reference materials to verify the accuracy of the procedure are available. The minor modifications to the ACOSA method introduced for this study are discussed at the end of this appendix.

Scope

This method determines the bitumen, water and solids content of test portions of oil sand in the range of 50 to 500 g.

Summary

Test samples are separated into bitumen, water and solids by refluxing with toluene in a Modified Dean Stark Extractor shown in Figure B1. The bitumen and water are extracted from the solids by condensed solvent. The water is azeotropically distilled with the

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[a] The subcommittee responsible for development of this method was chaired by Dr. Jean Cooley, Syncrude Canada Research Ltd., Edmonton, Alberta

toluene and collected in the Dean Stark trap. The water is determined gravimetrically. The solids in the thimble are oven-dried and determined gravimetrically. The toluene-bitumen bottoms are transferred into a volumetric flask and made up to volume. An aliquot is taken, the toluene evaporated on a glass fibre filter paper and the bitumen determined gravimetrically.

Safety Considerations

Toluene - Moderately toxic by skin adsorption and inhalation.
- Possesses irritant and anesthetic properties.
- Highly flammable.

Apparatus

The following apparatus is used for the analysis of test samples up to 150 grams.

1. Condenser - An Allihn condenser, 30 cm long, 4 cm diameter, with a 24/40 standard taper-bottom joint protected by a teflon sleeve.
2. Flask - A 1000 ml round bottom flask. The neck was 270 mm long and 6 mm in diameter with a 55/50 standard taper female joint (Figure B2).
3. Still head - a combination of adapter and water trap containing a 55/50 standard taper male joint protected by a Teflon sleeve, two 24/40 standard taper female joints, a 24/40 Teflon stopper, and a

30-mL glass sidearm which terminates in a Teflon stopcock (Figure B3).

4. Fibreglass tape - 0.3 cm thick by 2.5 cm wide to insulate the neck of the flask and the top of the still head.
5. Thimble Basket - a basket made from 2 aluminum wires to hold the extraction thimble (Figure B4).
6. Solvent Distributor - an aluminum solvent distributor and locking ring to hold the thimble basket in place (Figure B5).
7. Heating Mantle - 1000 mL, 335 W.
8. Variable Transformer - 0 to 120-V output, 10 amp.
9. Beaker - 600 mL, graduated every 50 mL.
10. Powder Funnel - 75-mm diameter, stemless.
11. Funnel Support - a wire triangle that sits on top of the beaker.
12. Water Bottle - 70-mm high x 25-mm diameter snap cap vial.
13. Top Loading Balance - readable to ±0.01 g.
14. Volumetric flask - 500 mL, Class A.
15. 5-mL Class A pipet with bulb.
16. Syringe - 10 mL glass, Luer-lok tip.
17. 25-mL Erlenmeyer flask with ground glass neck, fitted with a ground glass stopper.
18. Petri dishes - 100-mm diameter, 100-mm deep.
19. Drying rack - a horizontal rod suspended between two retort stands approximately 1 m apart. Ten 20-mm fold back clips are hung on the rod.
20. Desiccator.
21. Analytical balance - readable to ±0.00001 g.

For 500-g test portions of oil sand the apparatus is scaled up by using a 2000-mL round bottom flask and increasing the size of the other components appropriately.

Materials and Reagents

1. Extraction Thimble - Whatman single thickness 43 x 123-mm cellulose thimble. A 33 x 80-mm extraction thimble is used for a 500 mL extraction apparatus and a 85 x 200-mm thimble is used for a 2000-mL extraction apparatus.
2. Phase Separation Filter Paper - 15-cm diameter Whatman IPS is suitable.
3. Toluene - Reagent Grade.
4. Glass fibre filter paper - 15-cm diameter, Whatman 934.AH or equivalent.

Procedure

1. Extraction thimbles are dried in a forced air oven at 105°C for 1 hour, then cooled in a desiccator.
2. For test portions of oil sand in the 50 to 150-gram range, 400 mL of toluene are placed in each of the round bottom flasks. For the larger samples and apparatus, approximately 900 mL are used.
3. The cooled extraction thimbles are weighed to the nearest 0.01 g. A test sample is transferred into each thimble and the unit re-weighed to the nearest 0.01 g. (Note: In this work test portions

which had been obtained by homogenization and subsampling of 1-kg lab samples were stored in 125-mL glass jars with screw caps until analysis. The jars were wiped clean with a pre-weighed tissue to remove residual bitumen and condensed water. The tissue was then extracted in a thimble with the oil sand. Where test portions were obtained by coring or halving of laboratory samples, subsampling was conducted just prior to extraction and intermediate containers were not used.)

4. Immediately after each test sample is transferred into a thimble, the thimble is placed in the wire basket. The basket is attached to the distributor and suspended from the bottom of the stillhead. The sidearm is filled with toluene, the condenser water turned on and the toluene heated to reflux by adjusting the heating mantle temperature with the Variac.
5. Periodically, the water and toluene are drained from the sidearm onto phase separating filter paper. After the toluene has filtered through and evaporated from the paper the water is quantitatively transferred to a collection bottle pre-weighed to the nearest 0.001 g. When extraction is complete the water bottle is re-weighed to the nearest 0.001 g and the weight of water in the sample obtained by difference.
6. Refluxing is continued until no further water is collected in the side-arm and the thimbles are no longer discolored by bitumen. (Note: This required 2 to 4 hours for the 50 g samples and up to 8 hours for the larger samples.)

7. After the extraction is complete the apparatus is cooled for approximately 30 minutes before disassembly. The extraction thimbles are dried in a forced-air oven at 105°C for 16 hours, cooled and re-weighed to the nearest 0.01 g to obtain the weight of retained solids.
8. The bitumen/toluene bottoms are transferred to 500-mL volumetric flasks, diluted to volume with toluene and mixed thoroughly.
9. Glass fibre filters, weighed to 0.00001 g, are supported on Petri dishes and 5-mL aliquots of the bitumen toluene solutions pipetted into the filters. The pipet tip is continually moved during delivery to ensure even dispersion of the extract over the surface. The filter is then hung on the drying rack in a fume hood for twenty minutes to remove solvent. (Note: This time was selected on the basis of previous experiments using standard bitumen-toluene solutions under the same conditions and with the same fumehood used in this work.) The dried filters are reweighed to the nearest 0.00001 g and the weight of bitumen obtained by difference. Bitumen weights are typically on the order of 0.04 to 0.15 g.

Calculations

The bitumen content of the oil sand is calculated by:

$$\text{Wt. Bitumen} = \frac{\text{wt. bitumen on filter paper}}{\text{volume of aliquot (5 mL)}} \times \begin{array}{l}\text{Volume of bitumen-}\\ \text{toluene solution}\end{array}$$

Component concentrations for oil sand are expressed as a percentage of the whole oil sand.

Discussion of the Analytical Method

In the absence of reference materials the accuracy of the analytical procedure is difficult to establish. There is however a consensus by industry that the method in principle is acceptable. The method described here deviates in several minor ways from the ACOSA method, but the changes are not judged to have a significant effect on the results of this study because the errors introduced are largely systematic in nature. Since the goal of this study was to improve the precision of the overall analysis, the presence of small systematic errors in the measurement step were of little consequence. Nevertheless, for the purpose of completeness a brief discussion of the errors arising from the analysis is included here.

% Bitumen and % Solids: During extraction of oil sand in cellulose thimbles some fine solids in the test sample may pass through the thimble into the bitumen extract, typically in an amount ranging from 0.1 to 0.4 % of the total sample. In the absence of procedures such as repeated centrifugation and washing with solvent, the values for solids are biased low while the bitumen values are high by an equivalent absolute amount. The magnitude of the bias varies from test portion to test portion within a bulk sample. However, the standard deviation of this bias is in the range of 0.1%.

In this work, the variability of the bias is accounted for in our estimate of s_a, the analytical standard deviation.

% Water: In most analyses the total of the bitumen, solids and water components is typically 99 to 100%. Loss of water during the extraction process contributes greatly to the fact that recovery of material is less than complete.

Because standard reference oil sands are not available for evaluation of the accuracy and precision of the determination of water, the only means of measuring loss is by pipetting known amounts of water into the extraction flask and carrying out an extraction (without oil sand). By distilling various amounts of water, 2.0 to 10.0 mL for example, a relation can be established between the absolute amount of water lost and the weight of water in the sample. On two separate occasions relations between the true and measured water levels in a test were established. These were:

$$\text{Corrected weight of water} = \frac{\text{Measured weight of water} + 0.22}{0.99}$$

$$\text{Corrected weight of water} = 1.003 \times \text{Measured weight of water} + 0.09$$

For a 100-g test portion of oil sand from which 3.00 g of water is collected, the first equation would correct the water content to 3.25% while the second would correct it to 3.10%. Clearly, there is appreciable scatter in the estimates of the bias. This is a reflection of the inconsistency in the water loss between extractors, between operators and from day to day as the temperature of the condenser water changes.

Rather than apply a constant water correction factor to a situation which is obviously variable, no correction was made. The extent of water loss is reflected by the fact that the total material balance from the assays in this work averaged above 99.5%. The random error associated with this bias is included in the precision statement for the determination of percent water, s_a.

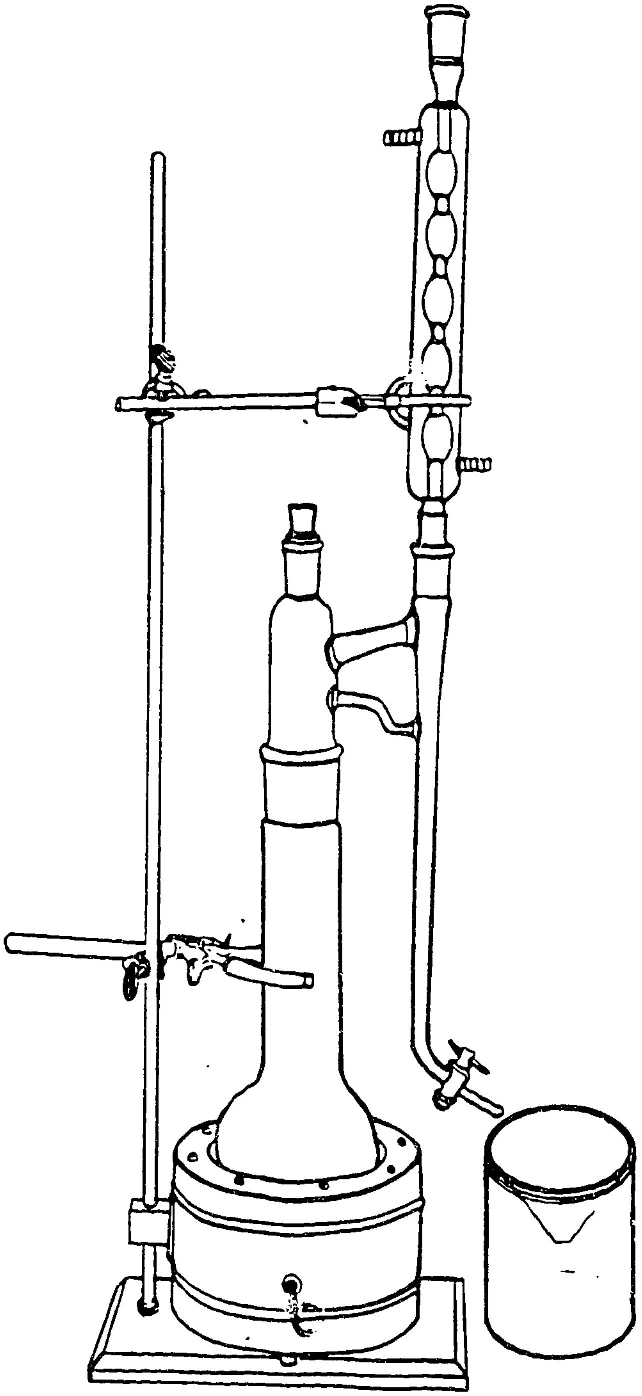

Figure B1: Modified Dean-Stark extraction apparatus

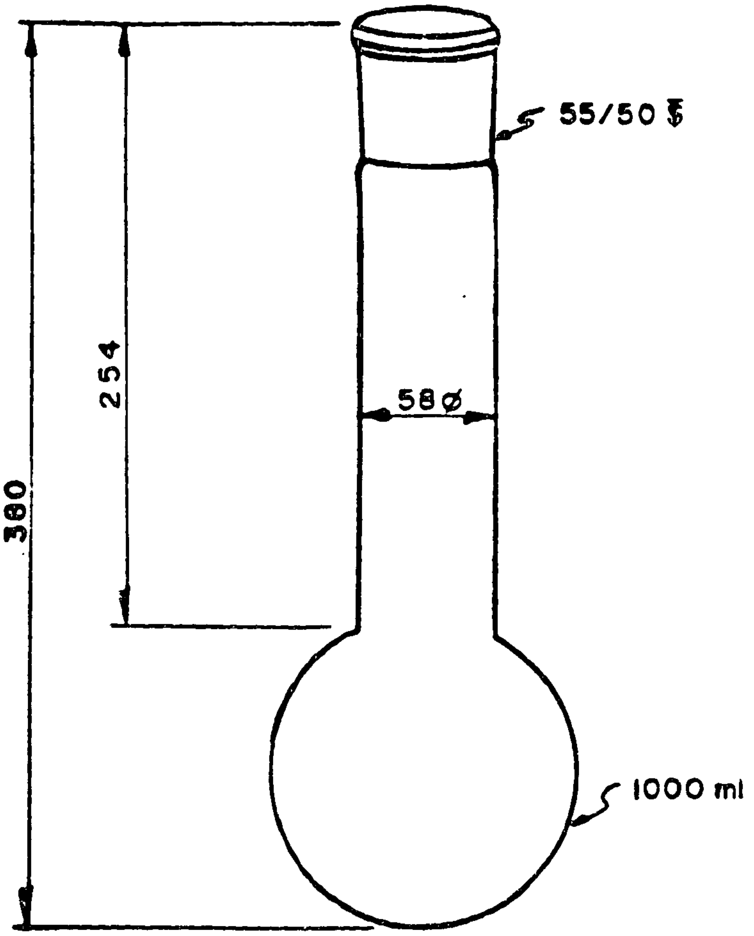

Figure B2: Extraction flask. Linear dimensions have units of millimeters.

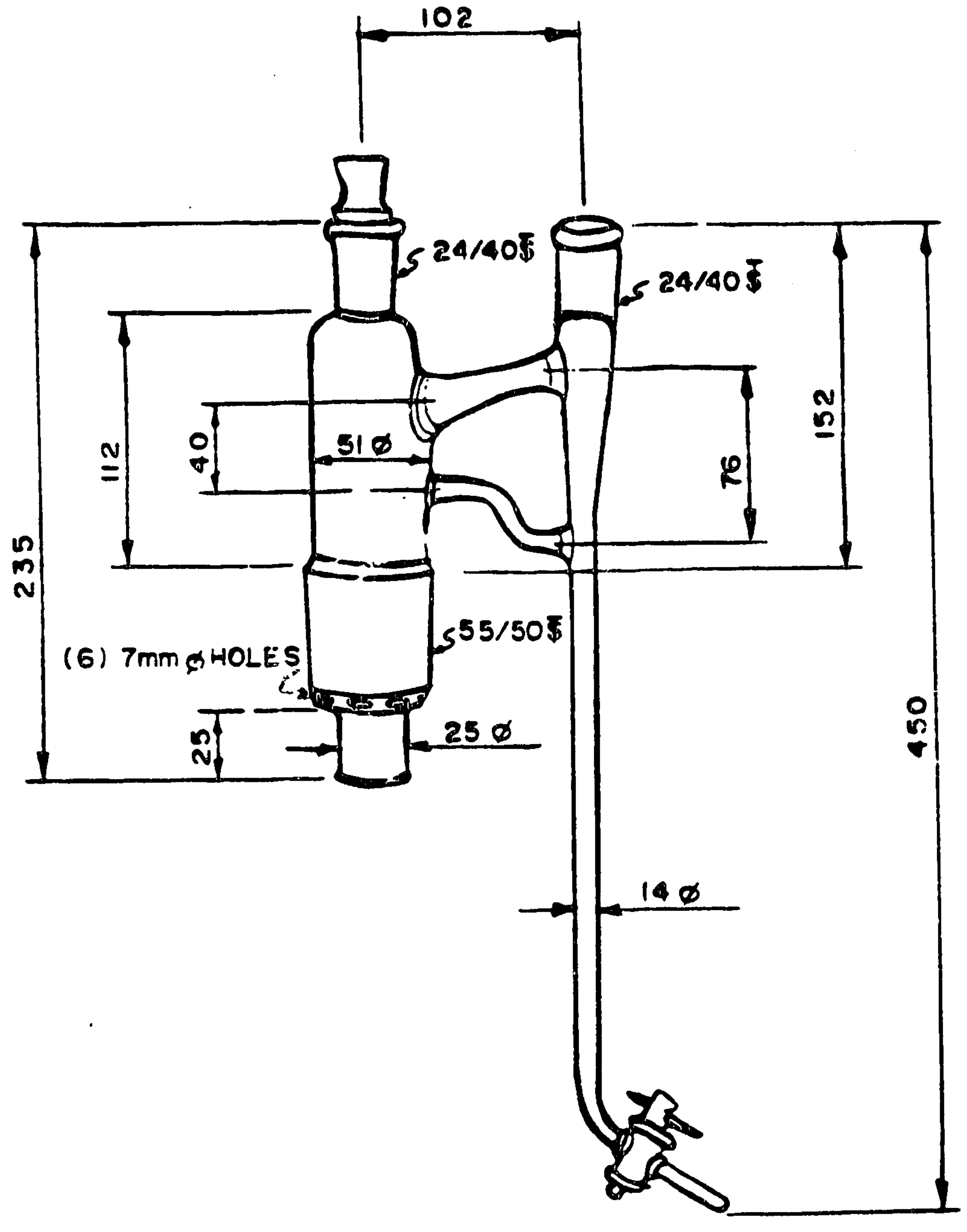

Figure B3: Dean Stark sidearm and stillhead for gravimetric determination of water. Linear dimensions have units of millimeters.

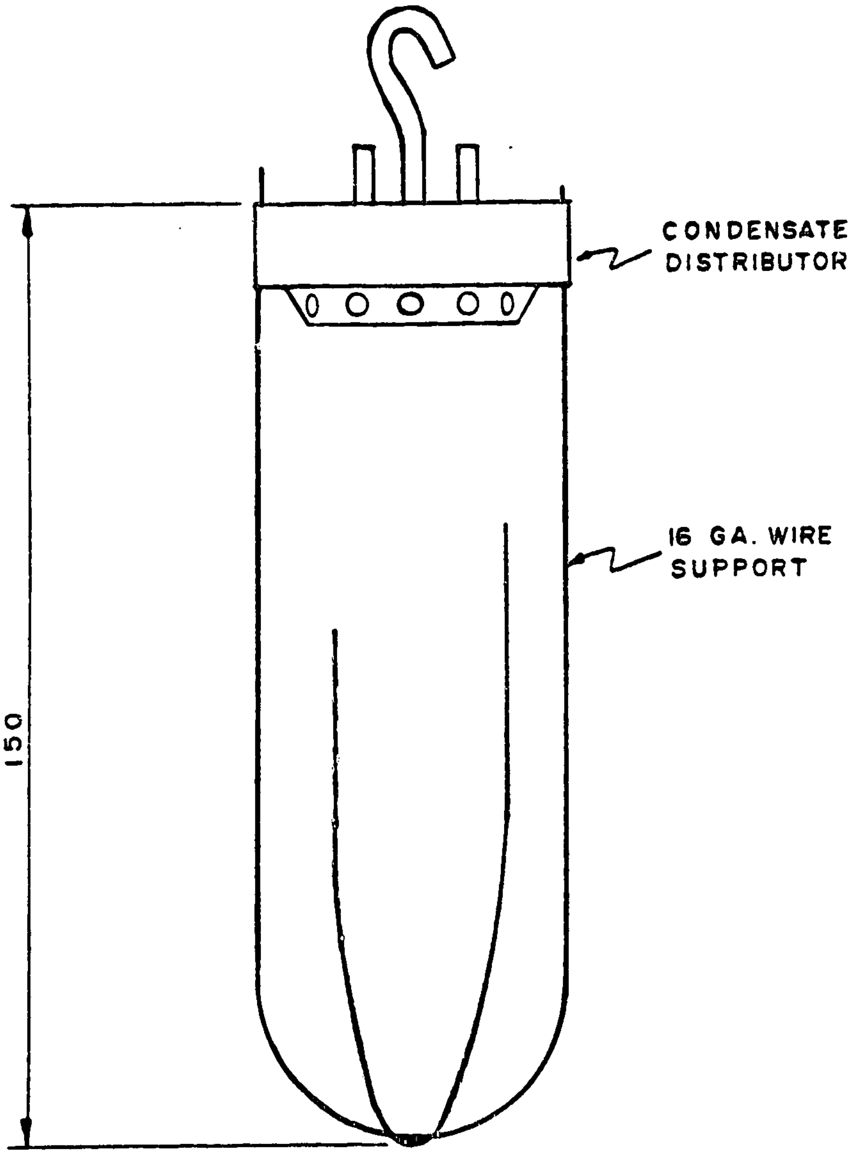

Figure B4: Basket support assembly. Linear dimensions have units of millimeters.

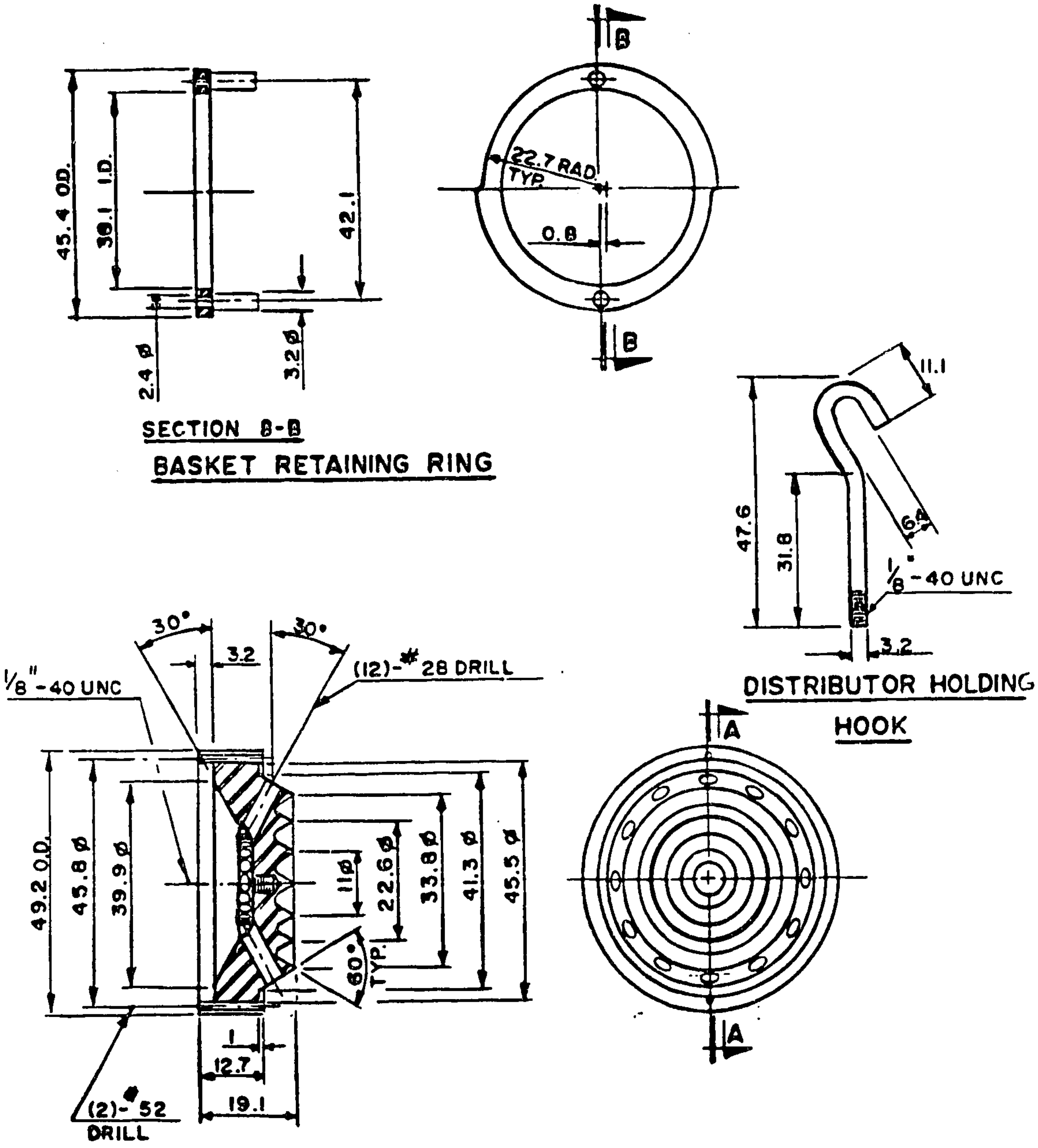

Figure B5: Condensate distributor. Linear dimensions have units of millimeters.

APPENDIX C

Evaluation of the Comil-Subsampler

Table C1: Final evaluation of the distribution of oil sand in the spinning sample collector. The second number in each column is the rank of the subsample weight with 1 representing the lightest, and 7 the heaviest, subsample.

	1A		1B		2A		2B		3A		3B		4A		4B		5A		5B		6A		6B	
Compartment	Wt. of Subsample (g)		Wt. of Subsample (g)		Wt. of Subsample (g)		Wt. of Subsample (g)		Wt. of Subsample (g)		Wt. of Subsample (g)		Wt. of Subsample (g)		Wt. of Subsample (g)		Wt. of Subsample (g)		Wt. of Subsample (g)		Wt. of Subsample (g)		Wt. of Subsample (g)	
1	139	5	139	6	136	6	130	5	140	6	138	4	139	7	131	3	125	3	135	5	126	2	138	6.5
2	136	3	126	1	118	1	130	5	120	1	128	1	137	5.5	129	2	126	4	137	6	132	4	123	1
3	141	6	137	5	141	7	134	7	129	3	132	3	136	4	141	7	137	7	142	7	134	5.5	137	5
4	134	1.5	130	2	128	3	123	1	126	2	130	2	131	1	125	1	131	6	128	3	134	5.5	132	2
5	146	7	136	4	134	4.5	128	3	134	4	145	7	137	5.5	137	4.5	127	5	127	2	138	7	136	4
6	134	1.5	131	3	134	4.5	126	2	147	7	143	6	132	2	137	4.5	124	2	121	1	125	1	133	3
7	138	4	145	7	125	2	130	5	139	5	141	5	134	3	139	6	123	1	134	4	130	3	138	6.5
x	138		135		131		129		134		137		135		134		128		132		131		134	
s	4.3		6.4		7.7		3.5		9.3		6.7		2.9		5.9		4.9		7.1		4.6		5.3	
RSD	3.1		4.7		5.9		2.7		6.9		4.9		2.2		4.4		3.8		5.4		3.6		4.0	

(continued)

	7A		7B		8A		8B		9		10		11		12		13		
Compartment	Wt. of Subsample (g)		Wt. of Subsample (g)		Wt. of Subsample (g)		Wt. of Subsample (g)		Wt. of Subsample (g)		Wt. of Subsample (g)		Wt. of Subsample (g)		Wt. of Subsample (g)		Wt. of Subsample (g)		Total Rank 1 to 3A
1	123	3	137	6	137	6	138	6	141	5.5	137	5	135	6.5	141	4.5	135	2.5	38
2	117	1	133	2	125	1	136	5	139	3.5	135	2.5	125	2	147	7	121	1	20.5
3	132	5	136	5	138	7	141	7	139	3.5	145	7	135	6.5	141	4.5	136	4	44.5
4	136	6	127	1	131	2	127	2	142	7	136	4	116	1	134	3	139	6	27
5	142	7	134	3	132	3	135	3.5	141	5.5	142	6	127	3	131	1.5	135	2.5	43
6	129	4	140	7	133	4	125	1	137	2	153	1	129	4.5	131	1.5	157	5	26
7	118	2	135	4	134	5	135	3.5	135	1	135	2.5	129	4.5	142	6	141	7	25
x	128		135		133		134		139		138		128		138		135		
s	9.3		4.0		4.3		5.8		2.5		4.3		6.5		6.2		6.5		
RSD	7.3		3.0		3.2		4.3		1.8		3.1		5.1		4.5		4.8		

Table C2: Estimation of the bias in the composition of subsamples

Trial No.	3A		3B		4B		6A		7B		8B		9		Mean (Rank No. 1)	Mean (Rank No. 7)	Difference No.1 - No.7
Subsample #	2	6	2	5	4	3	6	5	4	6	6	3	7	4			
Ranking	1	7	1	7	1	7	1	7	1	7	1	7	1	7			
% Bitumen	9.64	9.81	8.28	8.44	13.77	13.98	13.84	13.97	9.18	9.30	13.57	13.52	10.33	10.40	11.23	11.35	-0.12
% Solids	85.32	85.29	86.81	86.91	82.51	82.26	81.36	81.20	86.63	86.78	83.15	82.79	84.92	84.63	84.39	84.26	+0.13
% Water	4.74	4.74	4.39	4.46	3.35	3.56	4.48	4.42	3.99	3.64	2.91	3.36	4.28	4.50	4.02	4.10	-0.08

Table C3: Results of a factorial experiment to evaluate the Comil-spinning subsampler

Trial	Subsample unit #																				
	1			2			3			4			5			6			7		
	B	S	W	B	S	W	B	S	W	B	S	W	B	S	W	B	S	W	B	S	W
1A	8.98	86.73	4.09	8.74	87.03	3.98	8.95	86.87	4.02	---	--	---	---	---	---	8.87	87.11	3.74	---	---	---
1B	11.11	86.29	2.32	10.75	86.52	2.32	10.61	86.79	2.31	---	---	---	---	---	---	11.02	86.38	2.14	---	---	---
2A	14.13	80.11	5.47	---	---	---	14.04	80.31	5.33	---	---	---	---	---	---	14.04	80.33	5.17	14.12	80.43	5.03
2B	13.23	83.91	2.46	13.24	84.02	2.57	---	---	---	13.17	84.30	2.16	---	---	---	---	---	---	13.13	84.26	2.36
3A	---	---	---	9.64	85.32	4.74	9.73	85.23	4.36	---	---	---	---	---	---	9.81	85.29	4.74	9.67	85.57	4.51
3B	8.23	86.73	4.80	8.28	86.81	4.39	---	---	---	---	---	---	8.44	86.91	4.46	---	---	---	8.19	86.96	4.53
4A	13.81	82.69	3.25	13.73	82.90	3.13	---	---	---	---	---	---	---	---	---	13.77	82.86	2.97	13.69	82.78	3.03
4B	---	---	---	---	---	---	13.98	82.26	3.56	13.77	82.51	3.35	---	---	---	13.67	82.51	3.34	13.76	82.60	3.43
5A	8.81	85.38	5.61	8.67	85.44	5.63	---	---	---	8.72	85.49	5.35	8.83	85.36	5.54	---	---	---	---	---	---
5B	9.88	86.29	3.66	---	---	---	---	---	---	9.57	86.63	3.45	9.53	86.58	3.53	9.57	86.62	3.60	---	---	---
6A	13.98	81.01	4.61	---	---	---	13.96	81.04	4.66	---	---	---	13.97	81.20	4.42	13.84	81.36	4.48	---	---	---
6B	13.37	84.36	1.99	---	---	---	13.22	84.52	1.92	---	---	---	13.40	84.39	1.98	---	---	---	13.32	84.38	1.94
7A	8.95	85.95	4.84	8.92	86.01	4.82	---	---	---	---	---	---	---	---	---	8.90	86.00	4.86	8.81	86.24	4.86
7B	9.39	86.67	3.76	---	---	---	9.42	86.59	3.66	9.18	86.63	3.99	---	---	---	9.30	86.78	3.64	---	---	---
8A	13.86	82.09	3.84	13.70	82.08	3.95	---	---	---	13.84	82.27	3.58	13.72	82.35	3.58	---	---	---	---	---	---
8B	13.49	82.77	3.43	---	---	---	13.52	82.79	3.36	---	---	---	13.44	82.97	3.05	13.57	83.16	2.01	---	---	---

Table C4. Results of subsampling experiments on a variety of oil sands

Trial	Subsample unit #																				
	1			2			3			4			5			6			7		
	B	S	W	B	S	W	B	S	W	B	S	W	B	S	W	B	S	W	B	S	W
9	---	---	---	---	---	---	10.29	84.88	4.33	10.40	84.63	4.50	10.48	84.85	4.13	---	---	---	10.33	84.92	4.26
10	13.31	84.48	1.78	---	---	---	---	---	---	13.37	84.51	1.70	13.28	84.55	1.67	13.40	84.52	1.69	---	---	---
11	6.16	91.33	2.26	5.99	91.47	2.26	---	---	---	---	---	---	5.94	91.56	2.16	---	---	---	6.10	91.42	2.05
12	7.50	85.96	6.10	---	---	---	---	---	---	7.88	85.67	5.99	7.82	85.77	5.91	7.80	85.76	5.97	---	---	---
13	---	---	---	14.75	84.25	0.63	14.59	84.37	0.56	---	---	---	14.27	84.73	0.48	14.79	84.24	0.58	---	---	---

Table C5: Effect of operating conditions on maximum bias in the estimate of % solids in high-grade oil sand. Descriptions of the symbols and variables are provided in Table 3.

Trial	Mean	x_2	x_3	x_2x_3	T-1	T-2	$\bar{x}$	s
2	+	+	-	-	0.52	0.85	0.69	0.23
4	+	-	-	+	0.43	0.34	0.39	0.06
6	+	+	+	+	0.47	0.70	0.59	0.16
8	+	-	+	-	0.13	0.45	0.29	0.23
Sum+	1.96	1.28	0.88	0.98			s_{pooled}=0.18	
Sum-	0.00	0.68	1.08	0.98				
Diff.	1.96	0.60	-0.20	0.00				
Effect	0.49	0.30	-0.10	0.00				

Minimum significant effect,

$$[\min]_{95\%\ \text{confidence}} = ts\ (2/mk)^{1/2}$$
$$= 2.78 \times 0.18 \times (2/(2\times 2))^{1/2}$$
$$= 0.35$$
$$[\min]_{90\%\ \text{confidence}} = 2.13 \times 0.18 \times (2/(2\times 2))^{1/2}$$
$$= 0.27$$

Table C6: Effect of operating conditions on the maximum bias in the estimate of of % solids in low-grade oil sand

Trial	Mean	x_2	x_3	x_2x_3	T-1	T-2	$\bar{x}$	s
2	+	+	-	+	0.00	0.00	0.00	0.00
4	+	-	-	-	-0.07	-0.12	-0.10	0.04
6	+	+	+	-	-0.19	-0.26	-0.23	0.05
8	+	-	+	+	-0.05	-0.07	-0.06	0.01
Sum+	-0.39	-0.16	-0.10	-0.06			s_{pooled}=0.03	
Sum-	0.00	-0.23	-0.29	-0.33				
Diff.	-0.39	0.07	0.19	0.27				
Effect	-0.10	0.04	0.10	0.14				

Minimum significant effect,

$$[\text{min}]_{95\%\text{ confidence}} = ts\,(2/mk)^{1/2}$$
$$= 2.78 \times 0.03 \times (2/(2\text{x}2))^{1/2}$$
$$= 0.06$$
$$[\text{min}]_{90\%\text{ confidence}} = 2.13 \times 0.03 \times (2/(2\text{x}2))^{1/2}$$
$$= 0.05$$

Table C7: Effect of operating conditions on the maximum bias in the estimate of % water in high-grade oil sand

Trial	Mean	x_2	x_3	x_2x_3	T-1	T-2	$\bar{x}$	s
2	+	+	-	+	0.25	0.09	0.17	0.11
4	+	-	-	-	0.06	0.11	0.09	0.04
6	+	+	+	-	0.15	0.03	0.09	0.08
8	+	-	+	+	0.19	0.14	0.17	0.04
Sum+	0.52	0.26	0.26	0.34			s_{pooled}=0.07	
Sum-	0.00	0.26	0.26	0.18				
Diff.	0.52	0.00	0.00	0.16				
Effect	0.13	0.00	0.00	0.08				

Minimum significant effect,

$$[\text{min}]_{95\%\ \text{confidence}} = ts\ (2/mk)^{1/2}$$
$$= 2.78 \times 0.07 \times (2/(2\times2))^{1/2}$$
$$= 0.14$$

$$[\text{min}]_{90\%\ \text{confidence}} = 2.13 \times 0.07 \times (2/(2\times2))^{1/2}$$
$$= 0.11$$

Table C8: Effect of operating conditions on the maximum bias in the estimate of % water in low-grade oil sand

Trial	Mean	x_2	x_3	x_2x_3	T-1	T-2	$\ddot{x}$	s
2	+	+	-	+	0.11	0.05	0.08	0.04
4	+	-	-	-	0.20	0.19	0.20	0.01
6	+	+	+	-	0.22	0.15	0.19	0.05
8	+	-	+	+	0.11	0.19	0.15	0.06
Sum+	0.62	0.35	0.28	0.23			s_{pooled}=0.04	
Sum-	0.00	0.27	0.34	0.39				
Diff.	0.62	0.08	-0.06	-0.16				
Effect	0.16	0.02	-0.03	-0.08				

Minimum significant effect,

$$[\text{min}]_{95\%\ \text{confidence}} = ts\ (2/mk)^{1/2}$$
$$= 2.78 \times 0.04 \times (2/(2\times2))^{1/2}$$
$$= 0.08$$

$$[\text{min}]_{90\%\ \text{confidence}} = 2.13 \times 0.04 \times (2/(2\times2))^{1/2}$$
$$= 0.06$$

Table C9: Effect of operating conditions on the range of bitumen contents reported for four subsamples of high-grade oil sand

Trial	Mean	x_2	x_3	x_2x_3	T-1	T-2	$\bar{x}$	s
2	+	+	-	+	0.09	0.11	0.10	0.01
4	+	-	-	-	0.12	0.31	0.22	0.13
6	+	+	+	-	0.14	0.18	0.16	0.03
8	+	-	+	+	0.16	0.13	0.15	0.02
Sum+	0.63	0.37	0.31	0.25			s_{pooled}=0.07	
Sum-	0.00	0.26	0.32	0.38				
Diff.	0.63	0.11	-0.01	-0.13				
Effect	0.16	0.06	-0.01	-0.07				

Minimum significant effect,

$$[\text{min}]_{95\%\ \text{confidence}} = ts\ (2/mk)^{1/2}$$

$$= 2.78 \times 0.07 \times (2/(2\times2))^{1/2}$$

$$= 0.14$$

$$[\text{min}]_{90\%\ \text{confidence}} = 2.13 \times 0.07 \times (2/(2\times2))^{1/2}$$

$$= 0.11$$

Table C10: Effect of operating conditions on the range of bitumen contents reported for four subsamples of low-grade oil sand

Trial	Mean	x_2	x_3	x_2x_3	T-1	T-2	$\bar{x}$	s
2	+	+	-	+	0.24	0.60	0.42	0.25
4	+	-	-	-	0.17	0.25	0.21	0.06
6	+	+	+	-	0.16	0.35	0.26	0.13
8	+	-	+	+	0.14	0.24	0.19	0.07
Sum+	1.08	0.40	0.45	0.61			s_{pooled}=0.15	
Sum-	0.00	0.68	0.63	0.47				
Diff.	1.08	-0.28	-0.18	0.14				
Effect	0.27	-0.14	-0.09	-0.07				

Minimum significant effect,

$$[\text{min}]_{95\%\ \text{confidence}} = ts\ (2/mk)^{1/2}$$

$$= 2.78 \times 0.15 \times (2/(2\text{x}2))^{1/2}$$

$$= 0.29$$

$$[\text{min}]_{90\%\ \text{confidence}} = 2.13 \times 0.15 \times (2/(2\text{x}2))^{1/2}$$

$$= 0.23$$

Table C11: Effect of operating conditions on the range of solids contents reported for four subsamples of high-grade oil sand

Trial	Mean	x_2	x_3	x_2x_3	T-1	T-2	$\bar{x}$	s
2	+	+	-	+	0.32	0.39	0.36	0.05
4	+	-	-	-	0.21	0.25	0.23	0.03
6	+	+	+	-	0.35	0.16	0.26	0.13
8	+	-	+	+	0.27	0.38	0.33	0.08
Sum+	1.18	0.56	0.59	0.69			$s_{pooled}=0.08$	
Sum-	0.00	0.62	0.59	0.49				
Diff.	1.18	-0.06	0.00	0.20				
Effect	0.30	-0.30	0.00	0.10				

Minimum significant effect,

$$[\mathrm{min}]_{95\%\ \mathrm{confidence}} = ts\,(2/mk)^{1/2} = 2.78 \times 0.08 \times (2/(2\times2))^{1/2} = 0.16$$

$$[\mathrm{min}]_{90\%\ \mathrm{confidence}} = 2.13 \times 0.08 \times (2/(2\times2))^{1/2} = 0.12$$

Table C12: Effect of operating conditions on the range of solids contents reported for four subsamples of low-grade oil sand

Trial	Mean	x_2	x_3	x_2x_3	T-1	T-2	$\bar{x}$	s
2	+	+	-	+	0.38	0.44	0.44	0.08
4	+	-	-	-	0.34	0.23	0.29	0.08
6	+	+	+	-	0.13	0.34	0.24	0.15
8	+	-	+	+	0.29	0.19	0.24	0.07
Sum+	1.21	0.53	0.48	0.68			s_{pooled}=0.10	
Sum-	0.00	0.68	0.73	0.53				
Diff.	1.21	-0.15	-0.25	0.15				
Effect	0.30	0.08	-0.13	0.08				

Minimum significant effect,

$[\text{min}]_{95\%\ \text{confidence}} = ts\ (2/mk)^{1/2}$

$= 2.78 \times 0.10 \times (2/(2\times2))^{1/2}$

$= 0.20$

$[\text{min}]_{90\%\ \text{confidence}} = 2.13 \times 0.10 \times (2/(2\times2))^{1/2}$

$= 0.15$

Table C13: Effect of operating conditions on the range of water content reported for four subsamples of high-grade oil sand

Trial	Mean	x_2	x_3	x_2x_3	T-1	T-2	$\bar{x}$	s
2	+	+	-	+	0.44	0.41	0.43	0.02
4	+	-	-	-	0.28	0.22	0.25	0.04
6	+	+	+	-	0.24	0.07	0.16	0.12
8	+	-	+	+	0.37	0.52	0.45	0.11
Sum+	1.29	0.70	0.61	0.88			s_{pooled}=0.08	
Sum-	0.00	0.59	0.68	0.41				
Diff.	1.29	0.11	-0.07	0.47				
Effect	0.32	0.06	-0.04	0.24				

Minimum significant effect,

$$[\mathrm{min}]_{95\%\ \mathrm{confidence}} = ts\ (2/mk)^{1/2}$$

$$= 2.78 \times 0.08 \times (2/(2\times2))^{1/2}$$

$$= 0.16$$

$$[\mathrm{min}]_{90\%\ \mathrm{confidence}} = 2.13 \times 0.08 \times (2/(2\times2))^{1/2}$$

$$= 0.12$$

Table C14: Effect of operating conditions on the range of water content reported for four subsamples of low-grade oil sand

Trial	Mean	x_2	x_3	x_2x_3	T-1	T-2	$\bar{x}$	s
2	+	+	-	+	0.35	0.18	0.27	0.12
4	+	-	-	-	0.38	0.41	0.40	0.02
6	+	+	+	-	0.28	0.21	0.25	0.05
8	+	-	+	+	0.20	0.35	0.28	0.11
Sum+	1.20	0.68	0.53	0.55			s_{pooled}=0.09	
Sum-	0.00	0.52	0.67	0.65				
Diff.	1.20	0.16	-0.14	-0.10				
Effect	0.30	0.08	-0.07	0.05				

Minimum significant effect,

$$[\text{min}]_{95\%}\ \text{confidence} = ts\ (2/mk)^{1/2}$$
$$= 2.78 \times 0.09 \times (2/(2\times2))^{1/2}$$
$$= 0.18$$
$$[\text{min}]_{90\%}\ \text{confidence} = 2.13 \times 0.09 \times (2/(2\times2))^{1/2}$$
$$= 0.14$$

APPENDIX D

Evaluation of Subsampling and Analytical Uncertainty Specifically for the Oil Sands Used in the Sampling Study

Table D1: Determination of subsampling plus analytical uncertainty (s_{ss+a}) for % bitumen in high-grade oil sand

Sample	T-1	T-2	Mean	Standard deviation
1-1-1	14.60	14.66	14.630	0.042
1-1-4	13.36	13.38	13.370	0.014
1-1-23	14.46	14.80	14.630	0.240
1-2-18	14.30	14.36	14.330	0.042
1-3-2	13.97	13.98	13.975	0.007
1-3-26	11.91	11.98	11.945	0.049
1-4-13	15.18	14.72	14.950	0.325
1-4-27	12.60	12.91	12.755	0.219
1-4-32	14.91	14.72	14.815	0.134
1-4-34	14.05	14.07	14.060	0.014
1-5-10	15.11	14.78	14.945	0.233
1-5-19	15.59	15.06	15.325	0.375
			Pooled Std.Dev.	0.19

Analysis of variance

Source	DF	SS	MS	F	Parameters estimated
Sampling	11	22.0857	2.0078	55.89	$2s_s^2 + s^2_{ss+a}$
Subsampling plus analysis	12	0.4311	0.0359		s^2_{ss+a}
TOTAL	23	22.5168			

$s_{ss+a} = 0.19$ $s_s = 0.99$

Table D2: Determination of subsampling plus analytical uncertainty (s_{ss+a}) for % solids in high-grade oil sand

Sample	T-1	T-2	Mean	Standard deviation
1-1-1	83.72	83.75	83.735	0.021
1-1-4	84.32	84.34	84.330	0.014
1-1-23	84.07	84.22	84.145	0.106
1-2-18	83.49	83.37	83.430	0.085
1-3-2	83.92	84.09	84.005	0.120
1-3-26	84.52	84.37	84.445	0.106
1-4-13	83.58	84.01	83.795	0.304
1-4-27	84.63	84.76	84.695	0.092
1-4-32	83.66	83.85	83.755	0.134
1-4-34	84.12	84.26	84.190	0.099
1-5-10	83.02	83.56	83.290	0.382
1-5-19	83.63	84.12	83.875	0.346
			Pooled Std.Dev.	0.19

Analysis of variance

Source	DF	SS	MS	F	Parameters estimated
Sampling	11	3.7012	0.3365	9.21	$2s_s^2 + s^2_{ss+a}$
Subsampling plus analysis	12	0.4383	0.0365		s^2_{ss+a}
TOTAL	23	4.1394			

$s_{ss+a} = 0.19$ $s_s = 0.37$

Table D3: Determination of subsampling plus analytical uncertainty (s_{ss+a}) for % water in high-grade oil sand

Sample	T-1	T-2	Mean	Standard deviation
1-1-1	1.30	1.37	1.335	0.050
1-1-4	1.86	1.63	1.745	0.163
1-1-23	0.94	0.92	0.930	0.014
1-4-27	2.41	2.32	2.365	0.064
1-2-18	1.78	1.82	1.800	0.028
1-3-2	1.61	1.50	1.555	0.078
1-3-26	3.15	3.25	3.200	0.071
1-4-13	0.93	0.85	0.890	0.057
1-4-32	0.99	0.75	0.870	0.170
1-4-34	1.41	1.19	1.300	0.156
1-5-10	1.39	1.32	1.355	0.050
1-5-19	0.42	0.28	0.350	0.099
			Pooled Std.Dev.	0.10

Analysis of variance

Source	DF	SS	MS	F	Parameters estimated
Sampling	11	12.57634	1.14330	120.93	$2s_s^2 + s^2_{ss+a}$
Subsampling plus analysis	12	0.11345	0.00945		s^2_{ss+a}
TOTAL	23	12.68979			

$s_{ss+a} = 0.10$ $s_s = 0.75$

Table D4: Determination of subsampling plus analytical uncertainty (s_{ss+a}) for % bitumen in low-grade oil sand

Sample	T-1	T-2	Mean	Standard deviation
2-1-18	8.20	8.23	8.215	0.021
2-1-20	8.44	8.41	8.425	0.021
2-1-27	8.60	8.55	8.575	0.035
2-1-29	8.18	8.26	8.220	0.057
2-2-17	7.60	7.53	7.565	0.050
2-3-7	8.74	8.68	8.710	0.042
2-3-32	8.56	8.69	8.625	0.092
2-3-33	9.62	9.37	9.495	0.177
2-4-29	9.08	8.95	9.015	0.092
2-5-10	9.63	9.54	9.585	0.064
2-5-30	9.29	9.42	9.355	0.092
2-5-31	8.94	9.08	9.010	0.099
			Pooled Std.Dev.	0.08

Analysis of variance

Source	DF	SS	MS	F	Parameters estimated
Sampling	11	7.75484	0.70499	105.68	$2s_s^2 + s^2_{ss+a}$
Subsampling plus analysis	12	0.08005	0.00667		s^2_{ss+a}
TOTAL	23	7.83489			

$s_{ss+a} = 0.08$ $s_s = 0.59$

Table D5: Determination of subsampling plus analytical uncertainty (s_{ss+a}) for % solids in low-grade oil sand

Sample	T-1	T-2	Mean	Standard deviation
2-1-18	86.44	86.86	86.650	0.297
2-1-20	86.74	86.78	86.760	0.028
2-1-27	86.83	86.77	86.800	0.042
2-1-29	86.56	86.72	86.640	0.113
2-2-17	85.47	85.52	85.495	0.035
2-3-7	86.42	86.39	86.405	0.021
2-3-32	86.55	86.50	86.525	0.035
2-3-33	86.38	86.48	86.430	0.071
2-4-29	86.08	86.31	86.195	0.163
2-5-10	83.89	84.04	83.965	0.106
2-5-30	84.51	84.51	84.510	0.000
2-5-31	84.15	84.18	84.165	0.021

Pooled Std.Dev. 0.11

Analysis of variance

Source	DF	SS	MS	F	Parameters estimated
Sampling	11	25.0363	2.2760	182.45	$2s_s^2 + s^2_{ss+a}$
Subsampling plus analysis	12	0.1497	0.0125		s^2_{ss+a}
TOTAL	23	25.1860			

$s_{ss+a} = 0.11$ $s_s = 1.06$

Table D6: Determination of subsampling plus analytical uncertainty (s_{ss+a}) for % water in low-grade oil sand

Sample	T-1	T-2	Mean	Standard deviation
2-1-18	4.97	4.81	4.890	0.113
2-1-20	4.41	4.61	4.510	0.141
2-1-27	4.37	4.53	4.450	0.113
2-1-29	4.72	4.86	4.790	0.099
2-2-17	6.58	6.75	6.665	0.120
2-3-7	4.64	4.66	4.650	0.014
2-3-32	4.56	4.44	4.500	0.085
2-3-33	3.75	3.97	3.860	0.156
2-4-29	4.52	4.56	4.540	0.028
2-5-10	6.02	6.02	6.020	0.000
2-5-30	5.71	5.83	5.770	0.085
2-5-31	6.49	6.45	6.470	0.028
			Pooled Std.Dev.	0.10

Analysis of variance

Source	DF	SS	MS	F	Parameters estimated
Sampling	11	17.89063	1.62642	177.03	$2s_s^2 + s^2_{ss+a}$
Subsampling plus analysis	12	0.11025	0.00919		s^2_{ss+a}
TOTAL	23	18.00087			

$s_{ss+a} = 0.10$ $s_s = 0.90$

APPENDIX E

Individual Test Results for 50-, 500- and 950-g Increments of High- and Low-Grade Athabasca Oil Sand

Table E1: Summary of analyses of 950-g samples of high-grade oil sand

	Weight (g)	% Bitumen	% Solids	% Water
1-1-1A	837.18	14.60	83.72	1.30
1-1-1B		14.66	83.75	1.37
1-1-4A	856.45	13.36	84.32	1.86
1-1-4B		13.38	84.34	1.63
1-1-9	904.58	13.60	84.70	1.29
1-1-10	821.51	13.54	84.56	1.20
1-1-12	886.37	14.44	84.19	1.02
1-1-17	843.47	14.08	83.82	0.53
1-1-18	895.85	15.19	83.45	1.52
1-1-20	891.70	14.14	84.36	1.20
1-1-23A	820.72	14.46	84.07	0.94
1-1-23B		14.80	84.22	0.92
1-1-27	906.09	13.68	83.96	2.02
1-1-30	857.13	14.88	83.99	1.10
1-1-32	920.74	14.37	83.20	2.03
1-1-33	875.96	14.89	83.45	1.09
1-1-37	915.50	14.39	82.84	2.35
1-2-12	926.07	15.27	83.51	0.84
1-2-14	1033.25	15.86	83.50	0.45
1-2-18A	941.34	14.30	83.49	1.78
1-2-18B		14.36	83.37	1.82
1-2-22	988.58	14.10	84.05	1.44
1-2-27	956.83	12.71	84.08	2.83
1-2-29	996.98	14.18	84.45	1.07
1-3-1	1027.36	14.52	84.01	1.19
1-3-2A	1002.04	13.97	83.92	1.61
1-3-2B		13.98	84.09	1.50
1-3-5	1004.38	13.76	83.94	1.86
1-3-7	980.68	16.07	83.05	0.59
1-3-8	977.18	16.45	82.77	0.43
1-3-9	985.70	15.30	83.92	0.32
1-3-11	972.73	14.95	83.11	1.38
1-3-17	917.63	15.51	82.86	1.32
1-3-18	986.71	13.86	84.47	1.03
1-3-21	1016.33	14.20	84.29	1.13
1-3-24	951.93	14.21	84.47	0.94
1-3-26A	989.12	11.91	84.52	3.15
1-3-26B		11.98	84.37	3.25
1-3-27	961.27	12.33	84.62	2.73
1-3-31	996.20	13.77	84.08	1.68
1-4-3	978.34	13.75	84.26	1.59
1-4-12	933.54	13.63	84.15	1.53
1-4-13A	1031.57	15.18	83.58	0.93
1-4-13B		14.72	84.01	0.85
1-4-21	1011.61	15.76	83.34	0.46
1-4-26	1018.23	12.28	84.71	2.66
1-4-27A	1017.55	12.60	84.63	2.41
1-4-27B		12.91	84.76	2.32

Table E1. (continued)

	Weight (g)	% Bitumen	% Solids	% Water
1-4-32A	1026.71	14.91	83.66	0.90
1-4-32B		14.72	83.85	0.75
1-4-34A	946.88	14.05	84.12	1.41
1-4-34B		14.07	84.26	1.19
1-5-10A	981.92	15.11	83.02	1.39
1-5-10B		14.78	83.56	1.32
1-5-19A	1005.03	15.59	83.63	0.42
1-5-19B		15.06	84.11	0.28
1-5-21	978.51	14.14	84.19	1.08
1-5-23	930.76	13.82	83.44	2.44
1-5-24	1016.46	15.53	83.56	0.49
1-5-38	970.90	13.86	83.70	1.18
$\bar{x}^a$	951.95	14.31	83.87	1.38
s^a	60.16	1.00	0.53	0.69

[a] Does not include samples labelled "B" from the duplicate analyses.

Table E2: Summary of analyses of 500-g samples of high-grade oil sand

	Weight (g)	% Bitumen	% Solids	% Water
1-1-2	496.38	14.51	83.83	1.20
1-1-3	512.98	12.89	83.86	3.14
1-1-15	499.71	12.67	83.96	3.48
1-1-5	514.02	13.82	84.18	2.07
1-1-16	494.20	14.14	84.46	0.93
1-1-19	452.90	14.92	83.32	1.21
1-1-22	494.81	13.46	84.09	2.21
1-1-28	498.12	13.98	83.35	2.51
1-1-39	498.10	14.92	83.03	1.83
1-2-1	513.27	14.93	83.32	1.59
1-2-11	502.32	15.10	83.57	1.14
1-2-17	496.25	14.40	83.43	1.92
1-2-20	498.61	12.99	84.01	2.97
1-2-24	507.44	11.59	84.73	4.22
1-2-25	483.55	14.60	83.65	1.54
1-2-26	520.00	14.54	83.70	1.62
1-2-31	499.80	14.89	83.55	1.35
1-2-33	489.90	13.78	83.48	2.11
1-3-6	504.97	14.58	83.88	1.35
1-3-10	491.48	16.16	82.49	1.14
1-3-12	500.90	14.15	83.68	1.96
1-3-15	514.90	15.01	82.97	1.37
1-3-16	494.77	15.94	83.21	0.62
1-3-19	504.22	13.71	83.49	2.71
1-3-20	493.08	14.90	83.87	1.27
1-3-22	502.71	11.86	84.63	3.35
1-3-25	491.18	14.59	83.85	1.44
1-3-33	488.01	14.22	84.03	1.57
1-3-36	494.30	14.14	84.02	1.61
1-3-37	511.54	15.16	83.29	1.22
1-4-1	507.22	14.26	83.79	1.98
1-4-2	506.19	14.60	83.26	1.87
1-4-4	499.95	13.49	83.72	2.59
1-4-7	505.63	14.89	83.45	1.54
1-4-14	509.16	15.25	83.15	1.43
1-4-15	506.89	15.58	83.03	1.21
1-4-18	508.78	13.93	84.00	1.88
1-4-22	510.42	14.83	83.37	1.45
1-4-24	509.33	13.68	84.21	1.94
1-4-37	509.18	13.68	83.93	2.15
1-5-5	497.74	14.35	83.23	2.31
1-5-13	486.88	15.12	83.14	1.48
1-5-20	501.88	15.04	83.44	1.19
1-5-25	500.42	14.81	83.18	1.77
1-5-26	505.20	15.69	82.59	1.52
1-5-27	511.32	13.23	84.93	1.77
1-5-30	493.93	14.36	83.36	1.88
1-5-39	501.24	14.08	83.73	2.11
$\bar{x}$	500.75	14.32	83.65	1.85
s	10.77	0.94	0.50	0.71

Table E3: Summary of analyses of 50-g samples of high-grade oil sand

	Weight (g)	% Bitumen	% Solids	% Water
1-1-6	52.61	16.26	82.70	1.00
1-1-7	51.42	14.81	83.49	0.84
1-1-8	51.07	12.56	85.06	1.72
1-1-11	51.17	14.54	83.35	1.27
1-1-13	55.00	14.01	83.27	2.12
1-1-21	51.88	12.29	83.23	3.89
1-1-31	47.10	12.51	82.76	4.22
1-1-36	49.72	14.40	83.35	1.49
1-1-38	48.52	13.93	83.35	1.98
1-2-2	44.64	14.51	83.51	1.06
1-2-5	51.25	15.26	82.95	1.19
1-2-8	54.13	16.12	82.65	0.75
1-2-9	54.02	16.39	82.51	1.61
1-2-10	51.85	16.33	82.30	0.67
1-2-13	44.85	15.04	83.12	1.10
1-2-15	52.42	15.29	83.31	0.69
1-2-21	54.03	4.82	85.66	8.92
1-2-28	48.90	13.08	83.21	2.91
1-2-39	51.29	14.28	83.76	1.46
1-3-3	50.98	15.37	83.13	1.04
1-3-4	49.70	15.99	82.69	0.63
1-3-13	50.89	12.92	83.42	3.35
1-3-14	51.86	14.60	82.74	1.88
1-3-23	52.75	12.54	84.42	2.91
1-3-28	50.04	11.95	84.25	3.19
1-3-29	48.29	12.89	83.74	2.40
1-3-34	53.32	14.28	83.78	2.06
1-3-39	50.87	12.80	83.86	2.67
1-4-8	52.72	14.78	82.91	1.61
1-4-10	50.49	12.84	84.12	2.53
1-4-16	45.38	13.88	83.47	1.86
1-4-36	46.99	14.39	83.85	1.02
1-4-25	47.73	12.75	83.83	2.61
1-4-28	49.69	11.83	83.88	3.66
1-4-29	50.49	12.76	83.36	2.98
1-4-31	45.20	12.43	83.67	1.29
1-5-2	49.71	13.16	80.91	5.24
1-5-11	49.89	14.34	83.32	1.67
1-5-12	50.06	13.56	83.78	1.93
1-5-15	51.46	14.99	82.55	1.76
1-5-16	51.32	15.42	83.09	1.57
1-5-17	50.28	15.55	83.00	0.81
1-5-18	50.57	14.42	83.17	1.39
1-5-22	46.75	12.41	83.49	3.54
1-5-29	50.63	15.18	82.68	1.35
1-5-31	49.21	15.16	82.91	1.16
1-5-33	51.33	15.58	82.50	1.86
1-5-35	51.04	14.48	82.54	2.07
$\bar{x}$	50.32	13.95	83.30	2.10
s	2.43	1.86	0.74	1.44

Table E4: Summary of analyses of 950-g samples of low-grade oil sand

	Weight (g)	% Bitumen	% Solids	% Water
2-1-9	947.98	8.15	86.81	4.49
2-1-11	1002.15	9.36	87.10	3.26
2-1-12	908.97	7.95	86.42	5.45
2-1-13	897.95	8.97	86.59	4.14
2-1-17	851.05	8.40	86.46	4.08
2-1-18A	916.17	8.20	86.44	4.97
2-1-19	947.98	8.15	86.81	4.49
2-1-20A	876.43	8.44	86.74	4.41
2-1-20B		8.41	86.78	4.61
2-1-26	913.92	9.13	86.56	4.09
2-1-27A	921.64	8.60	86.83	4.37
2-1-27B		8.55	86.77	4.53
2-1-29A	894.24	8.18	86.56	4.72
2-1-29B		8.26	86.72	4.86
2-1-31	928.17	7.91	86.69	4.97
2-2-2	981.30	8.07	86.79	4.94
2-2-17A	959.30	7.60	85.47	6.58
2-2-17B		7.53	85.52	6.75
2-2-22	983.33	8.67	85.88	5.22
2-2-27	952.59	9.13	86.25	4.27
2-2-30	900.52	7.99	85.48	6.31
2-2-33	964.58	7.71	85.79	6.28
2-2-39	993.66	8.18	85.55	3.01
2-3-1	1003.77	8.03	85.44	6.08
2-3-7A	963.49	8.74	86.42	4.64
2-3-7B		8.68	86.39	4.66
2-3-10	1013.34	6.59	86.04	7.93
2-3-11	977.01	8.17	86.34	5.30
2-3-12	952.30	8.22	84.13	4.64
2-3-15	959.44	8.59	86.78	4.30
2-3-16	1013.48	8.04	85.40	6.34
2-3-31	917.89	8.86	86.43	4.33
2-3-32A	928.71	8.56	86.55	4.56
2-3-32B		8.69	86.50	4.44
2-3-33A	940.27	9.62	86.38	3.75
2-3-33B		9.37	86.48	3.97
2-3-39	938.30	9.96	86.79	2.80
2-4-12	995.17	8.48	86.30	5.01
2-4-15	979.68	8.77	86.20	4.66
2-4-29A	962.01	9.08	86.08	4.52
2-4-29B		8.95	86.31	4.56
2-4-30	927.42	8.77	86.16	4.56
2-4-31	946.75	8.48	86.28	4.87
2-4-33	945.10	8.92	86.08	4.57
2-4-38	961.02	9.18	85.87	4.69
2-5-1	1000.39	8.47	84.49	6.77
2-5-10A	900.33	9.63	83.89	6.02
2-5-10B		9.54	84.04	6.02

Table E4. (continued)

	Weight (g)	% Bitumen	% Solids	% Water
2-5-13	1037.33	7.18	84.01	8.64
2-5-20	1026.54	7.36	83.93	8.40
2-5-21	985.31	8.46	84.49	6.66
2-5-23	977.59	7.06	83.66	8.89
2-5-27	972.09	8.45	83.52	7.49
2-5-28	811.35	9.65	86.60	3.31
2-5-30A	967.42	9.29	84.51	5.71
2-5-30B		9.42	84.51	5.83
2-5-31A	958.11	8.94	84.15	6.49
2-5-31B		9.08	84.18	6.45
2-5-32	943.86	9.34	85.23	5.09
2-5-36	981.84	8.71	84.54	6.56
x^{a}	951.69	8.51	85.77	5.27
s^{a}	44.91	0.70	1.01	1.42

[a] Does not include samples labelled "B" from the duplicate analyses.

Table E5: Summary of analyses of 500-g samples of low-grade oil sand

	Weight (g)	% Bitumen	% Solids	% Water
2-1-1	499.99	9.06	86.44	4.11
2-1-6	496.89	8.14	86.42	5.28
2-1-8	485.51	8.23	86.42	5.20
2-1-14	496.62	7.79	88.14	3.97
2-1-19	498.63	8.25	86.11	5.38
2-1-21	482.88	7.94	86.40	5.39
2-1-32	506.18	7.72	86.83	5.23
2-1-34	508.89	10.43	87.52	1.85
2-1-35	496.10	8.64	86.21	4.86
2-1-36	490.94	8.07	87.01	4.81
2-1-39	491.48	7.79	87.27	4.71
2-2-5	499.11	9.33	85.86	4.62
2-2-6	497.46	9.23	85.95	4.58
2-2-9	511.02	8.42	85.98	5.51
2-2-13	490.08	9.81	86.38	3.54
2-2-15	494.75	9.03	86.28	4.50
2-2-18	499.99	8.30	82.26	5.31
2-2-26	511.82	8.69	85.97	5.10
2-2-34	486.60	6.15	85.65	7.76
2-2-37	497.61	7.77	85.50	6.48
2-3-18	497.29	9.49	86.49	3.72
2-3-19	501.76	8.73	86.23	4.82
2-3-20	496.31	8.97	86.50	4.26
2-3-23	494.88	9.97	85.91	3.87
2-3-25	506.17	7.91	87.48	4.37
2-3-27	495.10	9.39	86.16	4.20
2-3-35	507.15	10.49	85.62	3.73
2-4-2	497.93	8.69	85.48	5.64
2-4-14	504.33	8.62	86.32	4.88
2-4-16	509.54	7.37	85.63	6.70
2-4-17	500.14	9.65	86.05	4.08
2-4-18	495.90	8.13	85.82	5.72
2-4-24	500.90	9.37	85.38	5.02
2-4-27	494.04	8.35	86.08	5.43
2-4-32	510.99	8.48	86.10	5.11
2-4-36	491.76	8.89	86.25	4.69
2-5-2	508.48	7.39	84.05	8.34
2-5-3	504.70	7.73	84.04	7.89
2-5-4	512.55	8.22	84.44	7.06
2-5-6	496.41	9.08	84.44	6.28
2-5-7	500.18	8.56	84.59	6.55
2-5-8	511.80	8.36	84.11	7.24
2-5-11	509.03	7.78	84.18	7.70
2-5-14	514.49	7.95	83.68	7.95
2-5-15	505.38	8.13	84.04	7.68
2-5-26	496.80	11.27	84.58	3.86
2-5-37	504.26	10.10	84.86	4.89
2-5-39	507.13	7.66	83.57	8.68
$\bar{x}$	500.37	8.62	85.76	5.38
s	7.59	0.94	1.06	1.46

Table E6: Summary of analyses of 50-g samples of low-grade oil sand

	Weight (g)	% Bitumen	% Solids	% Water
2-1-2	48.82	9.56	85.01	4.23
2-1-3	50.82	7.59	86.07	6.27
2-1-10	49.16	6.98	85.80	6.17
2-1-15	50.19	9.39	86.37	4.05
2-1-16	50.24	8.30	85.83	4.84
2-1-30	45.91	7.43	86.19	5.53
2-1-37	48.31	6.91	87.21	5.84
2-2-7	48.43	11.07	86.06	2.58
2-2-10	47.22	8.00	86.38	5.63
2-2-11	50.98	6.70	85.52	7.39
2-2-14	52.84	8.13	84.39	6.36
2-2-20	57.16	7.82	86.00	5.94
2-2-21	53.84	8.78	86.61	4.15
2-2-29	48.82	9.30	85.33	4.47
2-2-32	51.33	8.10	85.55	5.32
2-2-35	56.39	5.34	85.39	8.33
2-2-36	47.25	6.47	86.56	5.94
2-3-5	51.21	9.11	84.48	5.44
2-3-8	50.26	8.43	86.85	4.62
2-3-9	48.91	7.76	87.86	4.33
2-3-14	49.02	8.06	86.33	5.44
2-3-17	48.78	10.60	85.65	2.84
2-3-21	45.78	9.35	86.85	3.44
2-3-24	49.04	9.62	85.62	3.76
2-3-28	53.32	7.21	86.33	5.61
2-3-29	47.96	9.19	86.80	3.66
2-3-30	51.31	5.01	87.29	6.73
2-3-34	54.65	9.02	86.97	3.19
2-3-36	48.71	7.85	85.36	6.64
2-4-6	47.98	8.41	86.54	4.87
2-4-10	53.83	7.93	85.58	6.43
2-4-13	51.22	7.36	85.92	6.57
2-4-21	49.18	8.31	86.09	5.66
2-4-23	45.80	9.45	86.70	3.18
2-4-25	49.92	8.37	85.68	5.16
2-4-26	47.38	8.08	85.84	4.90
2-5-5	53.09	7.77	83.93	8.10
2-5-9	55.32	6.82	84.07	8.35
2-5-12	54.13	11.14	83.39	4.48
2-5-16	53.34	7.77	82.62	8.52
2-5-17	50.78	6.34	83.64	9.16
2-5-18	53.87	7.29	82.85	8.96
2-5-19	52.02	7.59	83.16	9.16
2-5-24	47.64	7.49	83.35	8.76
2-5-29	45.83	7.91	84.77	6.36
2-5-33	48.36	10.11	86.10	2.87
2-5-34	57.01	9.92	87.46	2.48
2-5-38	56.59	6.57	81.34	11.31
$\bar{x}$	50.62	8.16	85.54	5.71
s	3.11	1.32	1.40	2.00

APPENDIX F

Summary of the Analysis of Neighboring Increments of High- and Low-Grade Oil Sand Used to Calculate an Intraclass Correlation Coefficient

Table F1: Neighbouring increments of high-grade oil sand

950-g samples		Bitumen (%)		Solids (%)		Water (%)	
1-1-4	1-1-9	13.36	13.60	84.32	84.70	1.86	1.29
1-1-17	1-1-18	14.08	15.19	83.82	83.45	0.53	1.52
1-1-20	1-1-27	14.14	13.68	84.36	83.96	1.20	2.02
1-1-32	1-1-33	14.37	14.89	83.20	83.45	2.03	1.09
1-2-12	1-2-18	15.27	14.30	83.51	83.49	0.84	1.78
1-3-1	1-3-2	14.52	13.97	84.01	83.92	1.19	1.61
1-3-5	1-3-11	13.76	14.95	83.94	83.11	1.86	1.38
1-3-7	1-3-8	16.07	16.45	83.05	82.77	0.59	0.43
1-3-17	1-3-18	15.51	13.86	82.86	84.47	1.32	1.03
1-3-26	1-3-27	11.91	12.33	84.52	84.62	3.15	2.73
1-4-12	1-4-13	13.63	15.18	84.15	83.58	1.53	0.93
1-4-26	1-4-32	12.28	14.91	84.71	83.66	2.66	0.99
1-4-21	1-4-27	15.76	12.60	83.34	84.63	0.46	2.41

500-g samples		Bitumen (%)		Solids (%)		Water (%)	
1-1-15	1-1-16	13.82	14.14	84.18	84.46	2.07	0.93
1-1-22	1-1-28	13.46	13.98	84.09	83.35	2.21	2.51
1-2-17	1-2-24	14.40	11.59	83.43	84.73	1.92	4.22
1-2-20	1-2-26	12.99	14.54	84.01	83.70	2.97	1.62
1-2-25	1-2-31	14.60	14.89	83.65	83.55	1.54	1.35
1-3-6	1-3-12	14.58	14.15	83.88	83.68	1.35	1.96
1-3-10	1-3-16	16.16	15.94	82.49	83.21	1.14	0.62
1-3-15	1-3-22	15.01	11.86	82.97	84.63	1.37	3.35
1-3-19	1-3-20	13.71	14.90	83.49	83.87	2.71	1.27
1-3-36	1-3-37	14.14	15.16	84.02	83.29	1.61	1.22
1-4-1	1-4-2	14.26	14.60	83.79	83.26	1.98	1.87
1-4-14	1-4-15	15.25	15.58	83.15	83.03	1.43	1.21
1-4-18	1-4-24	13.93	13.68	84.00	84.21	1.88	1.94
1-5-20	1-5-27	15.04	13.23	83.44	84.93	1.19	1.77
1-5-25	1-5-26	14.81	15.69	83.18	82.59	1.77	1.52

50-g samples		Bitumen (%)		Solids (%)		Water (%)	
1-1-6	1-1-7	16.26	14.81	82.70	83.49	1.00	0.84
1-1-31	1-1-36	12.51	14.40	82.76	83.35	4.22	1.49
1-2-8	1-2-9	16.12	16.39	82.65	82.51	0.75	1.61
1-2-15	1-2-21	15.29	4.81	83.31	85.66	0.69	8.92
1-3-3	1-3-4	15.37	15.99	83.13	82.69	1.04	0.63
1-3-13	1-3-14	12.92	14.60	83.42	82.74	3.35	1.88
1-3-23	1-3-29	12.54	12.89	84.42	83.74	2.91	2.40
1-3-34	1-3-39	14.28	12.80	83.78	83.86	2.06	2.67
1-4-10	1-4-16	12.84	13.88	84.12	83.47	2.53	1.86
1-4-28	1-4-29	11.83	12.76	83.88	83.36	3.66	2.98
1-4-25	1-4-31	12.75	12.43	83.83	83.67	2.61	1.29
1-5-11	1-5-17	14.34	15.55	83.32	83.00	1.67	0.81
1-5-12	1-5-18	13.56	14.42	83.78	83.17	1.93	1.39
1-5-15	1-5-16	14.99	15.42	82.55	83.09	1.76	1.57
1-5-29	1-5-35	15.18	14.48	82.68	82.54	1.35	2.07

Table F2: Neighbouring increments of low-grade oil sand

950-g samples		Bitumen (%)		Solids (%)		Water (%)	
2-1-11	2-1-17	9.36	8.40	87.10	86.46	3.26	4.08
2-1-12	2-1-18	8.20	7.95	86.42	86.44	5.45	4.97
2-1-13	2-1-20	8.44	8.97	86.59	86.74	4.14	4.41
2-1-26	2-1-27	9.13	8.60	86.56	86.83	4.09	4.37
2-2-27	2-2-33	9.13	7.71	86.25	85.79	4.27	6.28
2-3-11	2-3-12	8.17	8.22	86.34	84.13	5.30	4.64
2-3-10	2-3-16	8.04	6.59	86.04	85.40	7.93	6.34
2-3-31	2-3-32	8.86	8.56	86.43	86.55	4.33	4.56
2-4-30	2-4-31	8.77	8.48	86.16	86.28	4.56	4.87
2-4-33	2-4-38	9.18	8.92	86.08	85.87	4.57	4.69
2-5-20	2-5-21	7.36	8.46	83.93	84.49	8.40	6.66
2-5-27	2-5-28	9.65	8.45	83.52	86.60	7.49	3.31
2-5-30	2-5-31	9.29	8.94	84.51	84.15	5.71	6.49

500-g samples		Bitumen (%)		Solids (%)		Water (%)	
2-1-1	2-1-6	9.06	8.14	86.44	86.42	4.11	5.28
2-1-14	2-1-21	7.79	7.94	88.14	86.40	3.97	5.39
2-1-34	2-1-35	10.43	8.64	87.52	86.21	1.85	4.86
2-2-5	2-2-6	9.33	9.23	85.86	85.95	4.62	4.58
2-2-9	2-2-15	8.42	9.03	85.98	86.28	5.51	4.50
2-3-18	2-3-25	9.49	7.91	86.49	87.48	3.72	4.37
2-3-20	2-3-27	8.97	9.39	86.50	86.16	4.26	4.20
2-4-17	2-4-18	9.65	8.13	86.05	85.82	4.08	5.72
2-5-2	2-5-7	7.39	8.56	84.05	84.59	8.34	6.55
2-5-3	2-5-8	7.73	8.36	84.04	84.11	7.89	7.24
2-5-14	2-5-15	7.95	8.13	83.68	84.04	7.95	7.68

50-g samples		Bitumen (%)		Solids (%)		Water (%)	
2-1-2	2-1-3	9.56	7.59	85.01	86.07	4.23	6.27
2-1-10	2-1-16	6.98	8.30	85.80	85.83	6.17	4.84
2-2-14	2-2-20	8.13	7.82	84.39	86.00	6.36	5.94
2-2-29	2-2-35	9.30	5.34	85.33	85.39	4.47	8.33
2-3-8	2-3-9	8.43	7.76	86.85	87.86	4.62	4.33
2-3-17	2-3-24	10.60	9.62	85.65	85.62	2.84	3.76
2-3-28	2-3-29	7.21	9.19	86.33	86.80	5.61	3.66
2-4-25	2-4-26	8.37	8.08	85.68	85.84	5.16	4.90
2-5-17	2-5-24	6.34	7.49	83.64	83.35	9.16	8.76
2-5-18	2-5-19	7.29	7.59	82.85	83.16	8.96	9.16
2-5-33	2-5-38	10.11	6.57	86.10	81.34	2.87	11.31

APPENDIX G

Sampling Data from Model Populations in a One-Dimensional Array with Theoretical Degrees of Segregation Ranging from 0 to 1.0

Table G1: Sampling of a model population of $z = 1.0$ with 25% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2
1	0.448326	0.200996	0.422956	0.178892
3	0.422956	0.178892	0.449561	0.202105
7	0.434991	0.189217	0.448326	0.200996
11	0.398611	0.158891	0.419744	0.176185
15	0.430626	0.185439	0.427617	0.182856
19	0.424530	0.180226	0.400502	0.160402
23	0.424530	0.180226	0.429132	0.184154
27	0.404632	0.163727	0.413062	0.170620
31	0.430626	0.185439	0.438993	0.192715
35	0.400502	0.160402	0.444564	0.197637
39	0.460984	0.212506	0.432100	0.186710
43	0.434991	0.189217	0.437805	0.191673
47	0.450779	0.203202	0.433555	0.187970
49	0.432100	0.186710	0.437805	0.191673
99	0.437668	0.191553	0.444867	0.197907
149	0.418478	0.175124	0.452820	0.205046
199	0.442240	0.195576	0.416447	0.173428
249	0.439454	0.193120	0.446751	0.199586
299	0.437805	0.191673	0.442170	0.195514
349	0.412883	0.170472	0.423546	0.179391
399	0.429606	0.184561	0.441887	0.195264
449	0.433872	0.188245	0.429830	0.184754
499	0.447208	0.199995	0.416989	0.173880
549	0.432867	0.187374	0.429728	0.184666
599	0.444129	0.197251	0.443193	0.196420
649	0.414862	0.172110	0.414859	0.172108
699	0.431583	0.186264	0.442631	0.195922
749	0.422808	0.178767	0.425402	0.180967
799	0.427611	0.182851	0.419186	0.175717
849	0.428773	0.183846	0.422368	0.178395
899	0.445536	0.198502	0.444572	0.197644
949	0.446392	0.199266	0.426550	0.181945
999	0.437930	0.191783	0.404972	0.164002

Table G2: Sampling of a model population of $z = 0.8$ with 25% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2
1	0.439183	0.192882	0.409588	0.167762
3	0.390324	0.152353	0.377041	0.142160
7	0.367181	0.134822	0.335599	0.112627
11	0.357420	0.127749	0.355469	0.126358
15	0.353088	0.124671	0.347097	0.120476
19	0.358188	0.128299	0.347836	0.120990
23	0.336946	0.113533	0.344998	0.119024
27	0.328897	0.108173	0.352278	0.124100
31	0.363458	0.132102	0.341083	0.116338
35	0.355535	0.126405	0.329150	0.108340
39	0.358824	0.128755	0.320922	0.102991
43	0.356123	0.126824	0.355142	0.126126
47	0.345114	0.119104	0.343948	0.118300
49	0.349237	0.121966	0.358564	0.128568
99	0.321671	0.103472	0.343503	0.117994
149	0.337507	0.113911	0.346178	0.119839
199	0.346618	0.120144	0.350148	0.122604
249	0.344537	0.118706	0.350837	0.123087
299	0.348296	0.121310	0.338503	0.114584
349	0.351148	0.123305	0.326197	0.106404
399	0.334214	0.111699	0.355887	0.126656
449	0.330505	0.109234	0.354082	0.125374
499	0.319594	0.102140	0.352332	0.124138
549	0.350865	0.123106	0.355245	0.126199
599	0.336735	0.113390	0.340853	0.116181
649	0.354978	0.126009	0.324779	0.105481
699	0.350257	0.122680	0.351608	0.123628
749	0.344453	0.118648	0.347474	0.120738
799	0.349748	0.122324	0.346378	0.119978
849	0.354322	0.125544	0.337957	0.114215
899	0.342133	0.117055	0.330018	0.108912
949	0.342687	0.117434	0.345234	0.119187
999	0.350320	0.122724	0.350189	0.122632

Table G3: Sampling of a model population of $z = 0.6$ with 25% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2
1	0.411338	0.169199	0.434991	0.189217
3	0.327211	0.107067	0.327365	0.107168
7	0.270030	0.072916	0.284228	0.080786
11	0.264794	0.070116	0.269172	0.072454
15	0.275467	0.075882	0.272454	0.074231
19	0.268125	0.071891	0.272784	0.074411
23	0.266164	0.070843	0.265064	0.070259
27	0.272475	0.074243	0.256109	0.065592
31	0.255477	0.065268	0.269879	0.072835
35	0.249621	0.062311	0.271585	0.073758
39	0.246015	0.060523	0.274273	0.075226
43	0.280898	0.078904	0.272725	0.074379
47	0.255496	0.065278	0.263020	0.069180
49	0.269427	0.072591	0.268332	0.072002
99	0.261835	0.068558	0.242903	0.059002
149	0.259495	0.067338	0.254580	0.064811
199	0.265397	0.070436	0.262973	0.069155
249	0.264963	0.070205	0.257722	0.066421
299	0.255106	0.065079	0.261433	0.068347
349	0.242765	0.058935	0.262762	0.069044
399	0.267902	0.071771	0.248957	0.061980
449	0.265509	0.070495	0.248261	0.061634
499	0.266099	0.070809	0.238412	0.056840
549	0.266227	0.070877	0.264307	0.069858
599	0.255455	0.065257	0.251888	0.063448
649	0.242013	0.058570	0.267286	0.071442
699	0.264619	0.070023	0.263140	0.069243
749	0.262410	0.068859	0.259334	0.067254
799	0.259604	0.067394	0.262536	0.068925
849	0.253118	0.064069	0.265731	0.070613
899	0.248452	0.061728	0.254922	0.064985
949	0.258809	0.066982	0.256757	0.065924
999	0.260231	0.067720	0.261926	0.068605

Table G4: Sampling of a model population of $z = 0.4$ with 25% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2
1	0.430626	0.185439	0.426084	0.181548
3	0.282891	0.080027	0.281816	0.079420
7	0.215494	0.046438	0.225308	0.050764
11	0.207738	0.043155	0.209609	0.043936
15	0.199117	0.039648	0.198569	0.039430
19	0.193737	0.037534	0.201910	0.040768
23	0.203811	0.041539	0.190124	0.036147
27	0.188360	0.035479	0.175443	0.030780
31	0.186076	0.034624	0.200891	0.040357
35	0.176480	0.031145	0.178713	0.031938
39	0.169632	0.028775	0.184851	0.034170
43	0.183943	0.033835	0.191170	0.036546
47	0.176581	0.031181	0.177901	0.031649
49	0.185217	0.034305	0.185243	0.034315
99	0.182546	0.033323	0.163667	0.026787
149	0.173998	0.030275	0.170857	0.029192
199	0.173691	0.030169	0.175167	0.030683
249	0.179148	0.032094	0.173544	0.030118
299	0.169447	0.028712	0.180241	0.032487
349	0.164410	0.027031	0.176361	0.031103
399	0.178648	0.031915	0.169210	0.028632
449	0.175899	0.030940	0.165540	0.027403
499	0.176296	0.031080	0.159765	0.025525
549	0.178352	0.031809	0.176761	0.031244
599	0.171675	0.029472	0.169900	0.028866
649	0.162020	0.026250	0.179066	0.032065
699	0.175451	0.030783	0.176416	0.031123
749	0.173973	0.030267	0.173416	0.030073
799	0.172720	0.029832	0.174703	0.030521
849	0.168799	0.028493	0.178365	0.031814
899	0.164839	0.027172	0.170862	0.029194
949	0.171676	0.029473	0.171229	0.029319
999	0.173162	0.029985	0.175448	0.030782

Table G5: Sampling of a model population of $z = 0.2$ with 25% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2
1	0.418105	0.174812	0.436407	0.190451
3	0.255977	0.065524	0.272160	0.074071
7	0.179072	0.032067	0.179138	0.032090
11	0.154484	0.023865	0.161010	0.025924
15	0.140245	0.019669	0.137137	0.018807
19	0.123982	0.015372	0.129957	0.016889
23	0.127937	0.016368	0.129547	0.016782
27	0.116780	0.013638	0.118328	0.014002
31	0.116615	0.013599	0.117966	0.013916
35	0.117165	0.013728	0.113455	0.012872
39	0.110522	0.012215	0.106098	0.011257
43	0.117178	0.013731	0.103840	0.010783
47	0.113342	0.012846	0.101156	0.010233
49	0.108614	0.011797	0.099482	0.009897
99	0.095048	0.009034	0.098689	0.009740
149	0.090831	0.008250	0.092738	0.008600
199	0.092913	0.008633	0.090023	0.008104
249	0.086784	0.007531	0.094114	0.008857
299	0.096079	0.009231	0.094645	0.008958
349	0.086612	0.007502	0.091422	0.008358
399	0.091100	0.008299	0.086383	0.007462
449	0.089197	0.007956	0.090229	0.008141
499	0.083107	0.006907	0.094425	0.008916
549	0.087396	0.007638	0.093244	0.008694
599	0.082373	0.006785	0.091235	0.008324
649	0.083725	0.007010	0.092951	0.008640
699	0.092251	0.008510	0.082090	0.006739
749	0.088728	0.007873	0.083512	0.006974
799	0.089552	0.008020	0.090682	0.008223
849	0.091194	0.008316	0.085809	0.007363
899	0.089385	0.007990	0.086926	0.007556
949	0.085814	0.007364	0.092692	0.008592
999	0.089288	0.007972	0.087428	0.007644

Table G6: Sampling of a model population of $z = 0.0$ with 25% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2
1	0.419744	0.176185	0.450779	0.203202
3	0.257171	0.066137	0.240665	0.057920
7	0.162107	0.026279	0.159487	0.025436
11	0.128420	0.016492	0.140700	0.019796
15	0.105996	0.011235	0.110004	0.012101
19	0.102108	0.010426	0.095385	0.009098
23	0.092962	0.008642	0.085769	0.007356
27	0.085308	0.007277	0.083869	0.007034
31	0.078486	0.006160	0.078704	0.006194
35	0.072574	0.005267	0.071946	0.005176
39	0.067693	0.004582	0.067875	0.004607
43	0.065217	0.004253	0.068655	0.004714
47	0.062450	0.003900	0.065762	0.004325
49	0.062316	0.003883	0.064599	0.004173
99	0.046705	0.002181	0.043840	0.001922
149	0.034278	0.001175	0.035360	0.001250
199	0.031137	0.000970	0.031474	0.000991
249	0.026437	0.000699	0.025512	0.000651
299	0.024447	0.000598	0.023720	0.000563
349	0.024028	0.000577	0.023081	0.000533
399	0.022391	0.000501	0.020177	0.000407
449	0.019615	0.000385	0.019888	0.000396
499	0.019652	0.000386	0.020235	0.000409
549	0.020402	0.000416	0.017659	0.000312
599	0.018694	0.000349	0.016335	0.000267
649	0.015492	0.000240	0.017853	0.000319
699	0.016179	0.000262	0.014695	0.000216
749	0.015705	0.000247	0.015184	0.000231
799	0.015146	0.000229	0.014546	0.000212
849	0.016449	0.000271	0.014925	0.000223
899	0.013270	0.000176	0.013504	0.000182
949	0.014422	0.000208	0.012691	0.000161
999	0.012967	0.000168	0.013279	0.000176

Table G7: Sampling of a model population of z = 1.0 with 2.5% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2
1	0.163740	0.026811	0.163740	0.026811
3	0.140175	0.019649	0.148489	0.022049
7	0.177546	0.031523	0.156320	0.024436
11	0.131289	0.017237	0.131289	0.017237
15	0.131289	0.017237	0.131289	0.017237
19	0.170801	0.029173	0.148489	0.022049
23	0.156320	0.024436	0.190222	0.036184
27	0.190222	0.036184	0.140175	0.019649
31	0.196205	0.038496	0.170801	0.029173
35	0.131289	0.017237	0.156320	0.024436
39	0.155538	0.024192	0.121705	0.014812
43	0.131289	0.017237	0.099623	0.009925
47	0.184011	0.033860	0.170801	0.029173
49	0.177546	0.031523	0.128780	0.016584
99	0.156512	0.024496	0.140216	0.019661
149	0.186673	0.034847	0.121705	0.014812
199	0.170801	0.029173	0.154403	0.023840
249	0.134291	0.018034	0.158094	0.024994
299	0.171008	0.029244	0.121704	0.014812
349	0.148671	0.022103	0.165090	0.027255
399	0.121855	0.014849	0.111242	0.012375
449	0.133658	0.017864	0.111242	0.012375
499	0.112068	0.012559	0.141803	0.020108
549	0.167578	0.028082	0.162339	0.026354
599	0.163940	0.026876	0.100506	0.010101
649	0.165376	0.027349	0.140598	0.019768
699	0.125697	0.015800	0.122774	0.015073
749	0.102790	0.010566	0.103629	0.010739
799	0.112931	0.012753	0.128226	0.016442
849	0.102589	0.010525	0.108582	0.011790
899	0.170216	0.028973	0.116233	0.013510
949	0.152454	0.023242	0.137027	0.018776
999	0.066630	0.004440	0.156723	0.024562

Table G8: Sampling of a model population of $z = 0.8$ with 2.5% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2
1	0.111242	0.012375	0.111241	0.012375
3	0.093450	0.008733	0.111943	0.012531
7	0.119860	0.014366	0.083743	0.007013
11	0.109794	0.012055	0.118531	0.014050
15	0.106484	0.011339	0.152065	0.023124
19	0.150347	0.022604	0.134197	0.018009
23	0.117364	0.013774	0.118699	0.014089
27	0.111882	0.012518	0.149798	0.022439
31	0.127253	0.016193	0.125348	0.015712
35	0.111247	0.012376	0.100121	0.010024
39	0.135990	0.018493	0.132071	0.017443
43	0.087054	0.007578	0.154488	0.023867
47	0.116269	0.013518	0.122999	0.015129
49	0.097668	0.009539	0.118147	0.013959
99	0.078665	0.006188	0.129168	0.016684
149	0.113779	0.012946	0.115263	0.013286
199	0.143811	0.020682	0.130311	0.016981
249	0.126929	0.016111	0.149744	0.022423
299	0.115072	0.013242	0.112056	0.012557
349	0.136242	0.018562	0.117087	0.013709
399	0.121512	0.014765	0.109819	0.012060
449	0.105189	0.011065	0.087517	0.007659
499	0.123578	0.015272	0.149177	0.022254
549	0.128416	0.016491	0.063678	0.004055
599	0.115415	0.013321	0.097408	0.009488
649	0.111705	0.012478	0.140207	0.019658
699	0.117942	0.013910	0.095825	0.009182
749	0.126506	0.016004	0.120158	0.014438
799	0.133373	0.017788	0.099388	0.009878
849	0.118879	0.014132	0.130831	0.017117
899	0.057202	0.003272	0.113500	0.012882
949	0.115542	0.013350	0.105296	0.011087
999	0.120196	0.014447	0.098454	0.009693

Table G9: Sampling of a model population of $z = 0.6$ with 2.5% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2
1	0.140176	0.019649	0.156320	0.024436
3	0.133789	0.017899	0.128299	0.016461
7	0.093988	0.008834	0.098497	0.009702
11	0.087104	0.007587	0.086495	0.007481
15	0.098354	0.009674	0.127001	0.016129
19	0.099915	0.009983	0.110443	0.012198
23	0.093519	0.008746	0.119208	0.014211
27	0.114246	0.013052	0.094052	0.008846
31	0.073927	0.005465	0.090660	0.008219
35	0.102745	0.010557	0.087512	0.007658
39	0.079616	0.006339	0.089987	0.008098
43	0.097215	0.009451	0.109812	0.012059
47	0.103204	0.010651	0.077471	0.006002
49	0.097813	0.009567	0.106409	0.011323
99	0.106635	0.011371	0.064992	0.004224
149	0.060880	0.003706	0.083331	0.006944
199	0.114882	0.013198	0.105372	0.011103
249	0.067091	0.004501	0.096846	0.009379
299	0.079148	0.006264	0.074718	0.005583
349	0.098736	0.009749	0.073270	0.005368
399	0.107396	0.011534	0.093801	0.008799
449	0.091485	0.008370	0.104462	0.010912
499	0.085430	0.007298	0.080807	0.006530
549	0.061683	0.003805	0.087389	0.007637
599	0.074579	0.005562	0.093605	0.008762
649	0.099334	0.009867	0.067978	0.004621
699	0.066488	0.004421	0.085312	0.007278
749	0.097079	0.009424	0.078880	0.006222
799	0.081412	0.006628	0.091229	0.008323
849	0.085095	0.007241	0.087655	0.007683
899	0.073876	0.005458	0.079385	0.006302
949	0.103614	0.010736	0.080852	0.006537
999	0.083341	0.006946	0.070466	0.004965

Table G10: Sampling of a model population of $z = 0.4$ with 2.5% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2
1	0.177547	0.031523	0.099623	0.009925
3	0.110692	0.012253	0.109678	0.012029
7	0.085127	0.007247	0.096896	0.009389
11	0.065073	0.004234	0.072246	0.005219
15	0.081790	0.006690	0.058201	0.003387
19	0.084498	0.007140	0.049181	0.002419
23	0.073861	0.005455	0.065022	0.004228
27	0.073477	0.005399	0.069247	0.004795
31	0.075318	0.005673	0.060931	0.003713
35	0.069378	0.004813	0.071999	0.005184
39	0.062840	0.003949	0.057898	0.003352
43	0.053716	0.002885	0.065393	0.004276
47	0.064059	0.004104	0.072416	0.005244
49	0.062284	0.003879	0.077432	0.005996
99	0.067383	0.004540	0.073018	0.005332
149	0.044108	0.001946	0.063581	0.004043
199	0.060744	0.003690	0.056209	0.003159
249	0.078652	0.006186	0.069673	0.004854
299	0.065264	0.004259	0.069698	0.004858
349	0.054214	0.002939	0.046190	0.002134
399	0.075815	0.005748	0.058159	0.003382
449	0.074410	0.005537	0.042828	0.001834
499	0.034699	0.001204	0.028771	0.000828
549	0.055081	0.003034	0.067632	0.004574
599	0.060083	0.003610	0.061081	0.003731
649	0.050546	0.002555	0.062954	0.003963
699	0.040662	0.001653	0.042634	0.001818
749	0.034050	0.001159	0.049352	0.002436
799	0.078089	0.006098	0.052150	0.002720
849	0.072839	0.005306	0.070901	0.005027
899	0.045453	0.002066	0.064333	0.004139
949	0.050838	0.002585	0.057422	0.003297
999	0.048995	0.002401	0.042893	0.001840

Table G11: Sampling of a model population of $z = 0.2$ with 2.5% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2
1	0.140176	0.019649	0.121705	0.014812
3	0.107618	0.011582	0.083733	0.007011
7	0.047406	0.002247	0.054649	0.002987
11	0.051683	0.002671	0.047295	0.002237
15	0.053271	0.002838	0.058310	0.003400
19	0.045904	0.002107	0.041081	0.001688
23	0.043231	0.001869	0.044618	0.001991
27	0.041832	0.001750	0.052299	0.002735
31	0.039996	0.001600	0.042377	0.001796
35	0.030730	0.000944	0.048346	0.002337
39	0.037261	0.001388	0.034532	0.001192
43	0.033398	0.001115	0.036072	0.001301
47	0.032698	0.001069	0.041765	0.001744
49	0.036021	0.001298	0.040048	0.001604
99	0.026739	0.000715	0.042905	0.001841
149	0.028098	0.000789	0.025583	0.000654
199	0.036243	0.001314	0.037115	0.001378
249	0.028138	0.000792	0.031390	0.000985
299	0.029402	0.000864	0.029627	0.000878
349	0.027716	0.000768	0.032520	0.001058
399	0.026889	0.000723	0.021869	0.000478
449	0.026939	0.000726	0.039944	0.001596
499	0.028265	0.000799	0.038200	0.001459
549	0.030061	0.000904	0.026254	0.000689
599	0.026295	0.000691	0.030968	0.000959
649	0.025891	0.000670	0.022780	0.000519
699	0.025408	0.000646	0.032809	0.001076
749	0.029352	0.000862	0.027585	0.000761
799	0.028152	0.000793	0.027339	0.000747
849	0.022356	0.000500	0.026775	0.000717
899	0.033760	0.001140	0.027591	0.000761
949	0.024346	0.000593	0.026606	0.000708
999	0.030461	0.000928	0.034222	0.001171

Table G12: Sampling of a model population of $z = 0.0$ with 2.5% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2
1	0.184011	0.033860	0.140175	0.019649
3	0.089706	0.008047	0.090544	0.008198
7	0.053374	0.002849	0.055535	0.003084
11	0.050269	0.002527	0.047340	0.002241
15	0.040078	0.001606	0.038525	0.001484
19	0.033839	0.001145	0.036680	0.001345
23	0.033661	0.001133	0.033894	0.001149
27	0.029759	0.000886	0.028871	0.000834
31	0.026491	0.000702	0.027501	0.000756
35	0.026015	0.000677	0.024922	0.000621
39	0.025692	0.000660	0.025332	0.000642
43	0.021717	0.000472	0.024221	0.000587
47	0.025452	0.000648	0.023041	0.000531
49	0.022110	0.000489	0.022074	0.000487
99	0.016007	0.000256	0.015936	0.000254
149	0.013203	0.000174	0.012760	0.000163
199	0.012038	0.000145	0.011179	0.000125
249	0.009973	0.000099	0.009216	0.000085
299	0.009452	0.000089	0.008615	0.000074
349	0.007850	0.000062	0.008133	0.000066
399	0.007735	0.000060	0.007722	0.000060
449	0.007420	0.000055	0.007356	0.000054
499	0.006935	0.000048	0.006849	0.000047
549	0.006890	0.000047	0.007019	0.000049
599	0.006385	0.000041	0.006567	0.000043
649	0.006178	0.000038	0.006081	0.000037
699	0.005794	0.000034	0.006342	0.000040
749	0.005774	0.000033	0.005517	0.000030
799	0.005350	0.000029	0.006124	0.000038
849	0.005489	0.000030	0.005191	0.000027
899	0.005243	0.000027	0.005795	0.000034
949	0.004710	0.000022	0.005338	0.000028
999	0.004918	0.000024	0.005208	0.000027

APPENDIX H

Sampling Data from Patchy Model Populations in a One-Dimensional Array

Table H1: Sampling of a model patchy population with one patch containing 25% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2	Theoretical Variance
1	0.448326	0.200996	0.422956	0.178892	0.1875
3	0.422956	0.178892	0.449561	0.202105	0.1875
7	0.434991	0.189217	0.448326	0.200996	0.1875
11	0.398611	0.158891	0.419744	0.176185	0.1875
15	0.430626	0.185439	0.427617	0.182856	0.1875
19	0.424530	0.180226	0.400502	0.160402	0.1875
23	0.424530	0.180226	0.429132	0.184154	0.1875
27	0.404632	0.163727	0.413062	0.170620	0.1875
31	0.430626	0.185439	0.438993	0.192715	0.1875
35	0.400502	0.160402	0.444564	0.197637	0.1875
39	0.460984	0.212506	0.432100	0.186710	0.1875
43	0.434991	0.189217	0.437805	0.191673	0.1875
47	0.450779	0.203202	0.433555	0.187970	0.1875
49	0.432100	0.186710	0.437805	0.191673	0.1875
99	0.437668	0.191553	0.444867	0.197907	0.1875
149	0.418478	0.175124	0.452820	0.205046	0.1875
199	0.442240	0.195576	0.416447	0.173428	0.1875
249	0.439454	0.193120	0.446751	0.199586	0.1875
299	0.437805	0.191673	0.442170	0.195514	0.1875
349	0.412883	0.170472	0.423546	0.179391	0.1875
399	0.429606	0.184561	0.441887	0.195264	0.1875
449	0.433872	0.188245	0.429830	0.184754	0.1875
499	0.447208	0.199995	0.416989	0.173880	0.1875
549	0.432867	0.187374	0.429728	0.184666	0.1875
599	0.444129	0.197251	0.443193	0.196420	0.1875
649	0.414862	0.172110	0.414859	0.172108	0.1875
699	0.431583	0.186264	0.442631	0.195922	0.1875
749	0.422808	0.178767	0.425402	0.180967	0.1875
799	0.427611	0.182851	0.419186	0.175717	0.1875
849	0.428773	0.183846	0.422368	0.178395	0.1875
899	0.445536	0.198502	0.444572	0.197644	0.1875
949	0.446392	0.199266	0.426550	0.181945	0.1875
999	0.437930	0.191783	0.404972	0.164002	0.1875

Table H2: Sampling of a model patchy population with two patches containing 25% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2	Theoretical Variance
1	0.443210	0.196435	0.437805	0.191673	0.1875
3	0.429132	0.184154	0.447073	0.199874	0.1875
7	0.432100	0.186710	0.427617	0.182856	0.1875
11	0.432100	0.186710	0.439183	0.192882	0.1875
15	0.436407	0.190451	0.434991	0.189217	0.1875
19	0.437805	0.191673	0.429132	0.184154	0.1875
23	0.424530	0.180226	0.432100	0.186710	0.1875
27	0.443210	0.196435	0.437805	0.191673	0.1875
31	0.426084	0.181548	0.419744	0.176185	0.1875
35	0.443210	0.196435	0.416447	0.173428	0.1875
39	0.419744	0.176185	0.462036	0.213477	0.1875
43	0.435352	0.189531	0.413062	0.170620	0.1875
47	0.450046	0.202541	0.451980	0.204286	0.1875
49	0.421359	0.177543	0.443210	0.196435	0.1875
99	0.414044	0.171432	0.445804	0.198741	0.1875
149	0.437322	0.191251	0.447300	0.200077	0.1875
199	0.435221	0.189417	0.419522	0.175999	0.1875
249	0.428535	0.183642	0.449902	0.202412	0.1875
299	0.422209	0.178260	0.426136	0.181592	0.1875
349	0.421606	0.177752	0.435697	0.189832	0.1875
399	0.446531	0.199390	0.415754	0.172851	0.1875
449	0.409745	0.167891	0.413955	0.171359	0.1875
499	0.434512	0.188801	0.433233	0.187691	0.1875
549	0.431299	0.186019	0.446921	0.199738	0.1875
599	0.418287	0.174964	0.426095	0.181557	0.1875
649	0.442945	0.196200	0.423827	0.179629	0.1875
699	0.389241	0.151509	0.420011	0.176409	0.1875
749	0.428195	0.183351	0.412558	0.170204	0.1875
799	0.447055	0.199858	0.400253	0.160202	0.1875
849	0.434323	0.188636	0.420174	0.176546	0.1875
899	0.416281	0.173290	0.427362	0.182638	0.1875
949	0.422368	0.178395	0.425643	0.181172	0.1875
999	0.396764	0.157422	0.410348	0.168385	0.1875

Table H3: Sampling of a model patchy population with four patches containing 25% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2	Theoretical Variance
1	0.453164	0.205358	0.432100	0.186710	0.1875
3	0.437805	0.191673	0.448326	0.200996	0.1875
7	0.443210	0.196435	0.440544	0.194079	0.1875
11	0.432100	0.186710	0.411337	0.169198	0.1875
15	0.409588	0.167762	0.407819	0.166316	0.1875
19	0.448252	0.200930	0.421811	0.177925	0.1875
23	0.439079	0.192790	0.445804	0.198741	0.1875
27	0.414636	0.171923	0.445134	0.198144	0.1875
31	0.432100	0.186710	0.437805	0.191673	0.1875
35	0.425854	0.181352	0.441515	0.194935	0.1875
39	0.434713	0.188975	0.445804	0.198741	0.1875
43	0.434746	0.189004	0.428086	0.183258	0.1875
47	0.433464	0.187891	0.422879	0.178827	0.1875
49	0.443080	0.196320	0.445457	0.198432	0.1875
99	0.426249	0.181688	0.432369	0.186943	0.1875
149	0.420798	0.177071	0.429028	0.184065	0.1875
199	0.443912	0.197058	0.437472	0.191382	0.1875
249	0.435668	0.189807	0.445606	0.198565	0.1875
299	0.436068	0.190155	0.413447	0.170938	0.1875
349	0.399546	0.159637	0.416508	0.173479	0.1875
399	0.452817	0.205043	0.440179	0.193758	0.1875
449	0.421747	0.177871	0.422409	0.178429	0.1875
499	0.430137	0.185018	0.418806	0.175398	0.1875
549	0.411156	0.169049	0.402428	0.161948	0.1875
599	0.421368	0.177551	0.430358	0.185208	0.1875
649	0.424305	0.180035	0.417020	0.173906	0.1875
699	0.446382	0.199257	0.427055	0.182376	0.1875
749	0.408828	0.167140	0.440129	0.193714	0.1875
799	0.413851	0.171273	0.406822	0.165504	0.1875
849	0.424267	0.180002	0.405419	0.164365	0.1875
899	0.418712	0.175320	0.414537	0.171841	0.1875
949	0.420592	0.176898	0.414649	0.171934	0.1875
999	0.415641	0.172757	0.397974	0.158383	0.1875

Table H4: Sampling of a model patchy population with eight patches containing 25% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2	Theoretical Variance
1	0.437805	0.191673	0.454330	0.206416	0.1875
3	0.439183	0.192882	0.427617	0.182856	0.1875
7	0.428965	0.184011	0.446862	0.199686	0.1875
11	0.437520	0.191424	0.440958	0.194444	0.1875
15	0.439005	0.192725	0.419744	0.176185	0.1875
19	0.427771	0.182988	0.436407	0.190451	0.1875
23	0.428630	0.183724	0.433026	0.187512	0.1875
27	0.439089	0.192799	0.397390	0.157919	0.1875
31	0.423717	0.179536	0.442720	0.196001	0.1875
35	0.422887	0.178833	0.430965	0.185731	0.1875
39	0.421766	0.177887	0.453384	0.205557	0.1875
43	0.437805	0.191673	0.435089	0.189302	0.1875
47	0.433235	0.187693	0.431521	0.186210	0.1875
49	0.417420	0.174239	0.428327	0.183464	0.1875
99	0.423243	0.179135	0.429206	0.184218	0.1875
149	0.413310	0.170825	0.415688	0.172797	0.1875
199	0.420416	0.176750	0.430097	0.184983	0.1875
249	0.439783	0.193409	0.384325	0.147706	0.1875
299	0.426601	0.181988	0.414322	0.171663	0.1875
349	0.412198	0.169907	0.427137	0.182446	0.1875
399	0.405746	0.164630	0.421294	0.177489	0.1875
449	0.432294	0.186878	0.419739	0.176181	0.1875
499	0.421861	0.177967	0.414242	0.171596	0.1875
549	0.372871	0.139033	0.401998	0.161602	0.1875
599	0.421942	0.178035	0.431583	0.186264	0.1875
649	0.405901	0.164756	0.408299	0.166708	0.1875
699	0.399516	0.159613	0.422941	0.178879	0.1875
749	0.407784	0.166288	0.407762	0.166270	0.1875
799	0.384330	0.147710	0.406343	0.165115	0.1875
849	0.412951	0.170529	0.399244	0.159396	0.1875
899	0.407576	0.166118	0.415569	0.172698	0.1875
949	0.400278	0.160222	0.416329	0.173330	0.1875
999	0.405643	0.164546	0.395917	0.156750	0.1875

Table H5: Sampling of a model patchy population with sixteen patches containing 25% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2	Theoretical Variance
1	0.441886	0.195263	0.411338	0.169199	0.1875
3	0.398546	0.158839	0.426084	0.181548	0.1875
7	0.454151	0.206253	0.437652	0.191539	0.1875
11	0.443210	0.196435	0.444896	0.197932	0.1875
15	0.425931	0.181417	0.423784	0.179593	0.1875
19	0.424811	0.180464	0.419881	0.176300	0.1875
23	0.436483	0.190517	0.427460	0.182722	0.1875
27	0.432322	0.186902	0.437803	0.191671	0.1875
31	0.444211	0.197323	0.427084	0.182401	0.1875
35	0.439770	0.193398	0.426588	0.181977	0.1875
39	0.410715	0.168687	0.412223	0.169928	0.1875
43	0.422548	0.178547	0.418249	0.174932	0.1875
47	0.417565	0.174361	0.394394	0.155547	0.1875
49	0.417752	0.174517	0.398851	0.159082	0.1875
99	0.438197	0.192017	0.452352	0.204622	0.1875
149	0.444459	0.197544	0.435635	0.189778	0.1875
199	0.424558	0.180249	0.420702	0.176990	0.1875
249	0.388851	0.151205	0.415468	0.172614	0.1875
299	0.425923	0.181410	0.414643	0.171929	0.1875
349	0.413034	0.170597	0.422140	0.178202	0.1875
399	0.392699	0.154213	0.410948	0.168878	0.1875
449	0.388656	0.151053	0.418705	0.175314	0.1875
499	0.392440	0.154009	0.394304	0.155476	0.1875
549	0.422625	0.178612	0.388973	0.151300	0.1875
599	0.398432	0.158748	0.377837	0.142761	0.1875
649	0.395292	0.156256	0.398890	0.159113	0.1875
699	0.413140	0.170685	0.411469	0.169307	0.1875
749	0.397803	0.158247	0.402079	0.161668	0.1875
799	0.385400	0.148533	0.400637	0.160510	0.1875
849	0.391073	0.152938	0.382894	0.146608	0.1875
899	0.389401	0.151633	0.365134	0.133323	0.1875
949	0.373800	0.139726	0.387916	0.150479	0.1875
999	0.375301	0.140851	0.366958	0.134658	0.1875

Table H6: Sampling of a model patchy population with thirty-two patches containing 25% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2	Theoretical Variance
1	0.436407	0.190451	0.443210	0.196435	0.187500
3	0.445804	0.198741	0.434991	0.189217	0.187500
7	0.439149	0.192852	0.439576	0.193227	0.187500
11	0.408373	0.166769	0.436407	0.190451	0.187500
15	0.433472	0.187898	0.440512	0.194051	0.187500
19	0.437110	0.191065	0.442106	0.195458	0.187500
23	0.418743	0.175346	0.436375	0.190423	0.187500
27	0.407573	0.166116	0.417142	0.174007	0.187500
31	0.428748	0.183825	0.417779	0.174539	0.187500
35	0.445048	0.198068	0.417484	0.174293	0.187500
39	0.428283	0.183426	0.434855	0.189099	0.187500
43	0.420463	0.176789	0.410498	0.168509	0.187500
47	0.429960	0.184866	0.428257	0.183404	0.187500
49	0.410127	0.168204	0.437559	0.191458	0.187500
99	0.425858	0.181355	0.427855	0.183060	0.187500
149	0.406135	0.164946	0.385424	0.148552	0.187500
199	0.403653	0.162936	0.416821	0.173740	0.187500
249	0.381958	0.145892	0.406765	0.165458	0.187500
299	0.397607	0.158091	0.386602	0.149461	0.187500
349	0.400271	0.160217	0.372414	0.138692	0.187500
399	0.352896	0.124536	0.394274	0.155452	0.187500
449	0.383987	0.147446	0.393885	0.155145	0.187500
499	0.360283	0.129804	0.365953	0.133922	0.187500
549	0.337979	0.114230	0.352551	0.124292	0.187500
599	0.360119	0.129686	0.361708	0.130833	0.187500
649	0.356293	0.126945	0.356857	0.127347	0.187500
699	0.342481	0.117293	0.358087	0.128226	0.187500
749	0.309498	0.095789	0.348815	0.121672	0.187500
799	0.317225	0.100632	0.337264	0.113747	0.183276
849	0.338539	0.114609	0.329051	0.108275	0.172482
899	0.320245	0.102557	0.288755	0.083379	0.162889
949	0.308303	0.095051	0.315366	0.099456	0.154307
999	0.308909	0.095425	0.315216	0.099361	0.146584

Table H7: Sampling of a model patchy population with sixty-four patches containing 25% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2	Theoretical Variance
1	0.426084	0.181548	0.454330	0.206416	0.187500
3	0.433555	0.187970	0.437805	0.191673	0.187500
7	0.426737	0.182104	0.440031	0.193627	0.187500
11	0.430630	0.185442	0.410834	0.168785	0.187500
15	0.431928	0.186562	0.443326	0.196538	0.187500
19	0.431547	0.186233	0.425342	0.180916	0.187500
23	0.426415	0.181830	0.408118	0.166560	0.187500
27	0.424836	0.180486	0.443318	0.196531	0.187500
31	0.431644	0.186317	0.412964	0.170539	0.187500
35	0.423217	0.179113	0.424531	0.180227	0.187500
39	0.420297	0.176650	0.405901	0.164756	0.187500
43	0.436924	0.190903	0.425955	0.181438	0.187500
47	0.443834	0.196989	0.430974	0.185739	0.187500
49	0.427191	0.182492	0.420644	0.176941	0.187500
99	0.407614	0.166149	0.408508	0.166879	0.187500
149	0.370061	0.136945	0.394394	0.155547	0.187500
199	0.394872	0.155924	0.398653	0.158924	0.187500
249	0.370035	0.136926	0.369889	0.136818	0.187500
299	0.339920	0.115546	0.349921	0.122445	0.187500
349	0.348524	0.121469	0.335422	0.112508	0.187500
399	0.325871	0.106192	0.333052	0.110924	0.183271
449	0.302552	0.091538	0.309100	0.095543	0.162862
499	0.299021	0.089414	0.294393	0.086667	0.146543
549	0.288295	0.083114	0.289787	0.083977	0.133197
599	0.275839	0.076087	0.272559	0.074288	0.122078
649	0.266083	0.070800	0.262458	0.068884	0.112673
699	0.249230	0.062116	0.256401	0.065741	0.104614
749	0.257782	0.066452	0.254093	0.064563	0.097630
799	0.237187	0.056258	0.244212	0.059640	0.091521
849	0.239865	0.057535	0.241876	0.058504	0.086131
899	0.231831	0.053746	0.225967	0.051061	0.081340
949	0.232703	0.054151	0.215866	0.046598	0.077055
999	0.207449	0.043035	0.217364	0.047247	0.073198

Table H8: Sampling of a model patchy population with one patch containing 2.5% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2	Theoretical Variance
1	0.163740	0.026811	0.163740	0.026811	0.024375
3	0.140175	0.019649	0.148489	0.022049	0.024375
7	0.177546	0.031523	0.156320	0.024436	0.024375
11	0.131289	0.017237	0.131289	0.017237	0.024375
15	0.131289	0.017237	0.131289	0.017237	0.024375
19	0.170801	0.029173	0.148489	0.022049	0.024375
23	0.156320	0.024436	0.190222	0.036184	0.024375
27	0.190222	0.036184	0.140175	0.019649	0.024375
31	0.196205	0.038496	0.170801	0.029173	0.024375
35	0.131289	0.017237	0.156320	0.024436	0.024375
39	0.155538	0.024192	0.121705	0.014812	0.024375
43	0.131289	0.017237	0.099623	0.009925	0.024375
47	0.184011	0.033860	0.170801	0.029173	0.024375
49	0.177546	0.031523	0.128780	0.016584	0.024375
99	0.156512	0.024496	0.140216	0.019661	0.024375
149	0.186673	0.034847	0.121705	0.014812	0.024375
199	0.170801	0.029173	0.154403	0.023840	0.024375
249	0.134291	0.018034	0.158094	0.024994	0.024375
299	0.171008	0.029244	0.121704	0.014812	0.024375
349	0.148671	0.022103	0.165090	0.027255	0.024375
399	0.121855	0.014849	0.111242	0.012375	0.024375
449	0.133658	0.017864	0.111242	0.012375	0.024375
499	0.112068	0.012559	0.141803	0.020108	0.024375
549	0.167578	0.028082	0.162339	0.026354	0.024375
599	0.163940	0.026876	0.100506	0.010101	0.024375
649	0.165376	0.027349	0.140598	0.019768	0.024375
699	0.125697	0.015800	0.122774	0.015073	0.024375
749	0.102790	0.010566	0.103629	0.010739	0.024375
799	0.112931	0.012753	0.128226	0.016442	0.024375
849	0.102589	0.010525	0.108582	0.011790	0.024375
899	0.170216	0.028973	0.116233	0.013510	0.024375
949	0.152454	0.023242	0.137027	0.018776	0.024375
999	0.066630	0.004440	0.156723	0.024562	0.024375

Table H9: Sampling of a model patchy population with two patches containing 2.5% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2	Theoretical Variance
1	0.163740	0.026811	0.170801	0.029173	0.024375
3	0.170801	0.029173	0.163740	0.026811	0.024375
7	0.184010	0.033860	0.163740	0.026811	0.024375
11	0.140175	0.019649	0.148489	0.022049	0.024375
15	0.148489	0.022049	0.175842	0.030920	0.024375
19	0.148489	0.022049	0.148542	0.022065	0.024375
23	0.177546	0.031523	0.190222	0.036184	0.024375
27	0.140176	0.019649	0.179453	0.032203	0.024375
31	0.140176	0.019649	0.186513	0.034787	0.024375
35	0.157040	0.024662	0.140176	0.019649	0.024375
39	0.148489	0.022049	0.140175	0.019649	0.024375
43	0.143429	0.020572	0.179828	0.032338	0.024375
47	0.164176	0.026954	0.177773	0.031603	0.024375
49	0.148489	0.022049	0.184010	0.033860	0.024375
99	0.147051	0.021624	0.131804	0.017372	0.024375
149	0.131186	0.017210	0.175153	0.030679	0.024375
199	0.171182	0.029303	0.138361	0.019144	0.024375
249	0.123388	0.015225	0.126901	0.016104	0.024375
299	0.136864	0.018732	0.110901	0.012299	0.024375
349	0.171162	0.029296	0.158386	0.025086	0.024375
399	0.140167	0.019647	0.153545	0.023576	0.024375
449	0.075554	0.005708	0.139035	0.019331	0.024375
499	0.130319	0.016983	0.165294	0.027322	0.024375
549	0.115751	0.013398	0.132342	0.017514	0.024375
599	0.154141	0.023759	0.135758	0.018430	0.024375
649	0.146460	0.021451	0.107348	0.011524	0.024375
699	0.151734	0.023023	0.167416	0.028028	0.024375
749	0.150903	0.022772	0.111399	0.012410	0.024375
799	0.123196	0.015177	0.170146	0.028950	0.024375
849	0.145856	0.021274	0.111910	0.012524	0.024375
899	0.170721	0.029146	0.129642	0.016807	0.024375
949	0.133986	0.017952	0.154322	0.023815	0.024375
999	0.154282	0.023803	0.145232	0.021092	0.024375

Table H10: Sampling of a model patchy population with four patches containing 2.5% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2	Theoretical Variance
1	0.131289	0.017237	0.140175	0.019649	0.024375
3	0.148489	0.022049	0.099623	0.009925	0.024375
7	0.121705	0.014812	0.170801	0.029173	0.024375
11	0.163740	0.026811	0.148523	0.022059	0.024375
15	0.121705	0.014812	0.163740	0.026811	0.024375
19	0.172587	0.029786	0.202430	0.040978	0.024375
23	0.198914	0.039567	0.156611	0.024527	0.024375
27	0.156316	0.024435	0.111242	0.012375	0.024375
31	0.184001	0.033856	0.148489	0.022049	0.024375
35	0.171385	0.029373	0.148489	0.022049	0.024375
39	0.121705	0.014812	0.129904	0.016875	0.024375
43	0.140175	0.019649	0.154813	0.023967	0.024375
47	0.148544	0.022065	0.163097	0.026601	0.024375
49	0.148489	0.022049	0.136432	0.018614	0.024375
99	0.147210	0.021671	0.150776	0.022733	0.024375
149	0.123345	0.015214	0.151915	0.023078	0.024375
199	0.143365	0.020554	0.150401	0.022620	0.024375
249	0.116931	0.013673	0.146666	0.021511	0.024375
299	0.136307	0.018580	0.145751	0.021243	0.024375
349	0.162144	0.026291	0.121598	0.014786	0.024375
399	0.186681	0.034850	0.131689	0.017342	0.024375
449	0.160645	0.025807	0.126089	0.015898	0.024375
499	0.138053	0.019059	0.133815	0.017906	0.024375
549	0.176988	0.031325	0.164407	0.027030	0.024375
599	0.091323	0.008340	0.139670	0.019508	0.024375
649	0.149356	0.022307	0.149958	0.022487	0.023474
699	0.135107	0.018254	0.114348	0.013075	0.021795
749	0.143262	0.020524	0.123321	0.015208	0.020340
799	0.119330	0.014240	0.136274	0.018571	0.019067
849	0.111872	0.012515	0.127136	0.016164	0.017944
899	0.110131	0.012129	0.112583	0.012675	0.016946
949	0.112741	0.012711	0.112733	0.012709	0.016053
999	0.106669	0.011378	0.119588	0.014301	0.015250

Table H11: Sampling of a model patchy population with eight patches containing 2.5% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2	Theoretical Variance
1	0.163740	0.026811	0.163740	0.026811	0.024375
3	0.148489	0.022049	0.156320	0.024436	0.024375
7	0.140176	0.019649	0.177546	0.031523	0.024375
11	0.148489	0.022049	0.174096	0.030309	0.024375
15	0.151756	0.023030	0.149178	0.022254	0.024375
19	0.103604	0.010734	0.131289	0.017237	0.024375
23	0.161954	0.026229	0.131289	0.017237	0.024375
27	0.148489	0.022049	0.183980	0.033849	0.024375
31	0.140277	0.019678	0.163740	0.026811	0.024375
35	0.114336	0.013073	0.156320	0.024436	0.024375
39	0.152990	0.023406	0.146497	0.021461	0.024375
43	0.116505	0.013573	0.111929	0.012528	0.024375
47	0.168746	0.028475	0.198134	0.039257	0.024375
49	0.131956	0.017412	0.138516	0.019187	0.024375
99	0.128100	0.016410	0.094199	0.008873	0.024375
149	0.103011	0.010611	0.114261	0.013056	0.024375
199	0.110491	0.012208	0.138057	0.019060	0.024375
249	0.132689	0.017606	0.148209	0.021966	0.024375
299	0.091886	0.008443	0.124883	0.015596	0.024375
349	0.122557	0.015020	0.093908	0.008819	0.021791
399	0.111848	0.012510	0.111930	0.012528	0.019060
449	0.099109	0.009823	0.112765	0.012716	0.016938
499	0.118299	0.013995	0.100436	0.010087	0.015240
549	0.118411	0.014021	0.112314	0.012614	0.013852
599	0.109811	0.012058	0.107013	0.011452	0.012696
649	0.093973	0.008831	0.118624	0.014072	0.011718
699	0.098884	0.009778	0.092124	0.008487	0.010880
749	0.093445	0.008732	0.106593	0.011362	0.010154
799	0.119330	0.014240	0.098757	0.009753	0.009518
849	0.072003	0.005184	0.079608	0.006337	0.008958
899	0.079988	0.006398	0.092948	0.008639	0.008459
949	0.090188	0.008134	0.085441	0.007300	0.008014
999	0.085050	0.007234	0.078208	0.006116	0.007613

Table H12: Sampling of a model patchy population with sixteen patches containing 2.5% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2	Theoretical Variance
1	0.163740	0.026811	0.177546	0.031523	0.024375
3	0.177546	0.031523	0.148489	0.022049	0.024375
7	0.140175	0.019649	0.144406	0.020853	0.024375
11	0.134861	0.018187	0.153721	0.023630	0.024375
15	0.105160	0.011059	0.140176	0.019649	0.024375
19	0.149455	0.022337	0.125546	0.015762	0.024375
23	0.149757	0.022427	0.143328	0.020543	0.024375
27	0.167188	0.027952	0.145732	0.021238	0.024375
31	0.154805	0.023965	0.153399	0.023531	0.024375
35	0.148489	0.022049	0.157023	0.024656	0.024375
39	0.157383	0.024769	0.172431	0.029732	0.024375
43	0.168267	0.028314	0.145925	0.021294	0.024375
47	0.180029	0.032410	0.140526	0.019748	0.024375
49	0.182170	0.033186	0.136594	0.018658	0.024375
99	0.158375	0.025083	0.123891	0.015349	0.024375
149	0.115892	0.013431	0.150559	0.022668	0.024375
199	0.116592	0.013594	0.113726	0.012934	0.019108
249	0.124055	0.015390	0.103253	0.010661	0.015271
299	0.105590	0.011149	0.114315	0.013068	0.012717
349	0.097506	0.009507	0.089630	0.008034	0.010895
399	0.085754	0.007354	0.101583	0.010319	0.009530
449	0.094401	0.008912	0.086538	0.007489	0.008469
499	0.077408	0.005992	0.080447	0.006472	0.007620
549	0.065958	0.004350	0.062400	0.003894	0.006926
599	0.068070	0.004634	0.077454	0.005999	0.006348
649	0.073704	0.005432	0.073633	0.005422	0.005859
699	0.072883	0.005312	0.067264	0.004524	0.005440
749	0.067204	0.004516	0.063957	0.004090	0.005077
799	0.068095	0.004637	0.062846	0.003950	0.004759
849	0.062317	0.003883	0.063688	0.004056	0.004479
899	0.062726	0.003935	0.055621	0.003094	0.004230
949	0.055972	0.003133	0.051726	0.002676	0.004007
999	0.057588	0.003316	0.052302	0.002735	0.003806

Table H13: Sampling of a model patchy population with thirty-two patches containing 2.5% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2	Theoretical Variance
1	0.148489	0.022049	0.156320	0.024436	0.024375
3	0.198679	0.039473	0.190222	0.036184	0.024375
7	0.131436	0.017275	0.140306	0.019686	0.024375
11	0.155641	0.024224	0.131664	0.017335	0.024375
15	0.163432	0.026710	0.163490	0.026729	0.024375
19	0.127610	0.016284	0.161146	0.025968	0.024375
23	0.162671	0.026462	0.160689	0.025821	0.024375
27	0.060023	0.003603	0.099120	0.009825	0.024375
31	0.100369	0.010074	0.068770	0.004729	0.024375
35	0.123805	0.015328	0.136895	0.018740	0.024375
39	0.165051	0.027242	0.113865	0.012965	0.024375
43	0.163320	0.026673	0.149126	0.022239	0.024375
47	0.094420	0.008915	0.106411	0.011323	0.024375
49	0.141782	0.020102	0.128904	0.016616	0.024375
99	0.087445	0.007647	0.110077	0.012117	0.019205
149	0.076682	0.005880	0.096268	0.009268	0.012760
199	0.078424	0.006150	0.079666	0.006347	0.009554
249	0.077795	0.006052	0.080196	0.006431	0.007636
299	0.071996	0.005183	0.075212	0.005657	0.006359
349	0.059233	0.003509	0.065235	0.004256	0.005448
399	0.067522	0.004559	0.061033	0.003725	0.004765
449	0.059726	0.003567	0.061547	0.003788	0.004234
499	0.055081	0.003034	0.056624	0.003206	0.003810
549	0.053901	0.002905	0.053224	0.002833	0.003463
599	0.048888	0.002390	0.048144	0.002318	0.003174
649	0.046389	0.002152	0.047169	0.002225	0.002930
699	0.044426	0.001974	0.042782	0.001830	0.002720
749	0.041834	0.001750	0.042396	0.001797	0.002538
799	0.041764	0.001744	0.042110	0.001773	0.002380
849	0.039748	0.001580	0.038218	0.001461	0.002239
899	0.038613	0.001491	0.039912	0.001593	0.002115
949	0.038100	0.001452	0.036914	0.001363	0.002003
999	0.037155	0.001380	0.036119	0.001305	0.001903

Table H14: Sampling of a model patchy population with sixty-four patches containing 2.5% of a component of interest

Increment size	Std. Dev. T-1	Variance T-1	Std. Dev. T-2	Variance T-2	Theoretical Variance
1	0.163740	0.026811	0.148489	0.022049	0.024375
3	0.162745	0.026486	0.135238	0.018289	0.024375
7	0.148953	0.022187	0.176709	0.031226	0.024375
11	0.156805	0.024588	0.123495	0.015251	0.024375
15	0.121550	0.014774	0.140314	0.019688	0.024375
19	0.153358	0.023519	0.134217	0.018014	0.024375
23	0.149148	0.022245	0.167154	0.027940	0.024375
27	0.145844	0.021270	0.111660	0.012468	0.024375
31	0.145206	0.021085	0.117588	0.013827	0.024375
35	0.144336	0.020833	0.126621	0.016033	0.024375
39	0.172814	0.029865	0.105737	0.011180	0.024375
43	0.103331	0.010677	0.113288	0.012834	0.022108
47	0.114323	0.013070	0.141593	0.020049	0.020226
49	0.099610	0.009922	0.129002	0.016642	0.019401
99	0.081750	0.006683	0.085059	0.007235	0.009602
149	0.075036	0.005630	0.071556	0.005120	0.006380
199	0.060732	0.003688	0.054496	0.002970	0.004777
249	0.059480	0.003538	0.058666	0.003442	0.003818
299	0.050146	0.002515	0.050589	0.002559	0.003179
349	0.045052	0.002030	0.045503	0.002071	0.002724
399	0.042589	0.001814	0.042174	0.001779	0.002383
449	0.038767	0.001503	0.038138	0.001455	0.002117
499	0.036375	0.001323	0.036232	0.001313	0.001905
549	0.033663	0.001133	0.033902	0.001149	0.001732
599	0.032194	0.001036	0.031335	0.000982	0.001587
649	0.030051	0.000903	0.029637	0.000878	0.001465
699	0.029508	0.000871	0.030679	0.000941	0.001360
749	0.028320	0.000802	0.027311	0.000746	0.001269
799	0.027838	0.000775	0.028343	0.000803	0.001190
849	0.027390	0.000750	0.027118	0.000735	0.001120
899	0.025397	0.000645	0.026484	0.000701	0.001057
949	0.025453	0.000648	0.025203	0.000635	0.001002
999	0.022173	0.000492	0.023360	0.000546	0.000952