Gy sampling theory in environmental studies. 1. Assessing soil splitting protocols[§]

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Five soil sample splitting methods (riffle splitting, paper cone riffle splitting, fractional shoveling, coning and quartering, and grab sampling) were evaluated with synthetic samples to verify Pierre Gy sampling theory expectations. Individually prepared samples consisting of layers of sand, NaCl and magnetite were left layered until splitting to simulate stratification from transport or density effects. Riffle splitting performed the best, with approximate 99% confidence levels of less than 2%, followed by paper cone riffle splitting. Coning and quartering and fractional shoveling were associated with significantly higher variability and also took much longer to perform. Common grab sampling was the poorest performer, with approximate 99% confidence levels of 100%–150% and biases of 15%–20%. Method performance rankings were in qualitative agreement with expectations from Gy sampling theory. Precision results depended on the number of increments, the type of increment, and other factors influencing the probability of selecting a particle at random, and were all much higher than Pierre Gy's fundamental error estimate of 1%. A critical factor associated with good performance for these methods is a low conditional probability of sampling adjacent particles. Accuracy levels were dominated by the sampling process rather than by the analytical method. Sampling accuracy was at least two orders of magnitude worse than the accuracy of the analytical method. Published in 2002 by John Wiley & Sons, Ltd.

KEYWORDS: sampling; sample splitting; subsampling; Gy sampling theory; particulate sampling; soil sampling

1. INTRODUCTION

Selecting a reduced sample mass from the quantity available for analysis is one of the most common procedures performed in an analytical laboratory. However, little attention is usually given to this procedure and the effect it may have on the quality of the data [1]. From a laboratory analyst's point of view, a reported sample concentration is an estimate of the average level of analyte in the original mass of sample received for analysis. For particulate or soil samples, this value is often based on the analysis of an aliquot selected from the sample. Subsampling practices have an important effect on the reported results. Improper subsampling procedures can lead to results that have significant biases and large imprecisions [2,3].

Schumacher *et al.* [4] compared homogenization methods including both closed- and open-bin riffle splitting and coning and quartering. They concluded that riffle splitting introduced the smallest level of inaccuracy despite the tendency for loss of fine particles, and that whatever method was used required a minimum of five passes before the inaccuracy of the sample estimate was minimized. Allen and Khan [5] compared five subsampling methods and found spinning and chute riffle splitting to perform much better than table sampling, scoop sampling or coning and quartering.

This study evaluated five laboratory splitting techniques as a component of an investigation of sampling effects in environmental studies by the United States Environmental Protection Agency (EPA), Las Vegas, NV. Test samples with stratified layers were used with no additional processing, simulating stratification effects that might occur during shipment from site to laboratory. The ability of each method to produce an accurate estimate of analyte level in the original sample was studied using a classical experimental design, and results are related to expectations from Pierre Gy sampling theory.

Gy sampling theory delineates seven classes of sampling error in addition to the error introduced by the analytical

method [2]. However, only four classes are relevant to this study: the fundamental error (FE), the grouping and segregation error (GE), the delimitation error (DE) and the extraction error (EE). The fundamental error is the expected variability due to the size and compositional distribution of the particles. It is determined by the sample characteristics and is independent of the sampling process. The grouping and segregation error is the contribution to uncertainty due to inhomogeneous analyte distributions within the sample. For instance, high-density particles with high levels of analyte often drop to lower levels of the sample, causing subsamples from the top to be biased low and subsamples from the bottom to be biased high.

The delimitation error arises when not every part of the sample has an equal chance of being selected. This error source affects grab sampling, but not the other subsampling techniques. The extraction error has to do with physically obtaining the sample from its original location, not extracting an analyte from a sample aliquot. If grab sampling specified the taking of a subsample at a particular location, the EE would represent the difference between what was targeted for removal and what was actually removed. For the methods used here, the EE is negligible.

2.   MATERIALS AND METHODS

Accuracy (inaccuracy) is defined to include information about both precision (a function of the standard deviation) and bias [6]. A distinction is also made between the terms sample splitting and subsampling. Sample splitting reduces a sample to *n* equal portions and attempts to maintain the same composition in each portion. Sample splitting techniques are commonly used to generate QA/QC samples and interlaboratory study samples. Subsampling can involve any procedure that produces an aliquot used in a chemical analysis. Subsampling does not require the original sample to be completely partitioned into a fixed number of aliquots. While sample splitting results in a subsample, subsampling does not necessarily produce a sample split. The only direct subsampling procedure described in this paper is grab sampling. For other analytical procedures the other sub-sampling methods must be revised to obtain the subsample mass required by each procedure from the sample mass received by the laboratory.

Sample splitting methods were applied to a set of laboratory-prepared samples. The composition and structure of the samples were controlled as much as possible and a very simple analyte scheme was devised to provide easily interpretable results. A detailed description of each protocol is provided because there are several variations on the application of any sample splitting protocol. A complete description is needed if one wants to compare results from this study with those from any other study. In addition, Gy sampling theory focuses on the importance of 'correct' sampling practices [1–3]. One cannot assess whether or not a method meets this standard without a comprehensive description.

Riffle splitting is designed to subsample dry, free-flowing material. The unstirred, layered sample was evenly poured into the feed hopper of a Jones-type riffle splitter
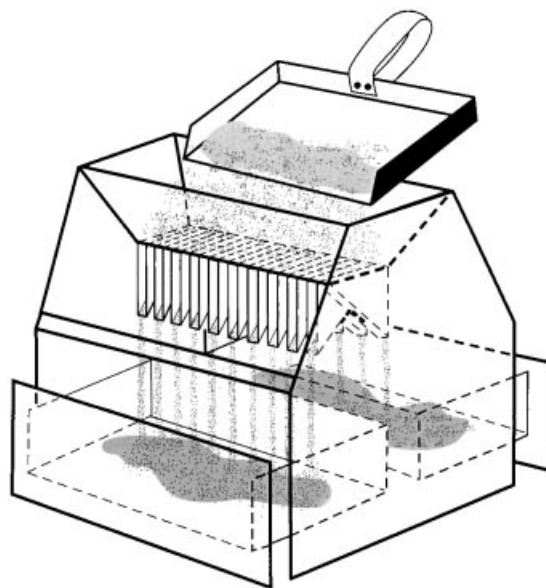

Figure 1. The basic components of a riffle splitter include the scoop, an even number of chutes, or riffles, and a pair of collection pans.

(21·6 cm × 27·9 cm hopper size, 1·27 cm riffle width, VWR #56720-060) (Figure 1). A small release gate drops the sample through the riffles into two receiving bins in one easy, reproducible and smooth operation. The contents of one bin were placed in a temporary holding container for later splitting. The other sample split was passed through the splitter until the sample was reduced to 5 g (after the fourth pass). No recombination of reject material was performed. The remaining rejects were passed through the splitter in the same manner until 16 5 g aliquots were obtained. This was a fast method, taking about 2 min to reduce an 80 g sample to 5 g aliquots.

Paper cone riffle splitting is a variation on conventional riffle splitting; it is also designed for subsampling dry, free-flowing materials. The availability of a conventional metal riffle splitter can be a problem with many laboratories, but paper is readily available. Riffle splitters reduce sample mass only by a factor of two per splitting stage. A paper cone riffle splitter can be used to reduce a sample by as much as a factor of eight per splitting stage, resulting in a more efficient size reduction. Paper cones can be used for one sample and discarded, eliminating cross-contamination and the cost of cleaning the apparatus between samples.

Construction of a paper cone splitter is very simple. A sheet of bond-quality paper is cut in the shape of an eight-sided star by placing a 15 cm × 15 cm square template in the center of the sheet, tracing the outline of the square, then rotating the template 45° and retracing the outline (Figure 2(a)). The paper is then clipped along the traced lines, folded downward in half along a line joining each opposing star point, and folded upward in half along a line joining opposing recessions between star points. The paper will then resemble a folded cone with troughs and ridges radiating from the center.
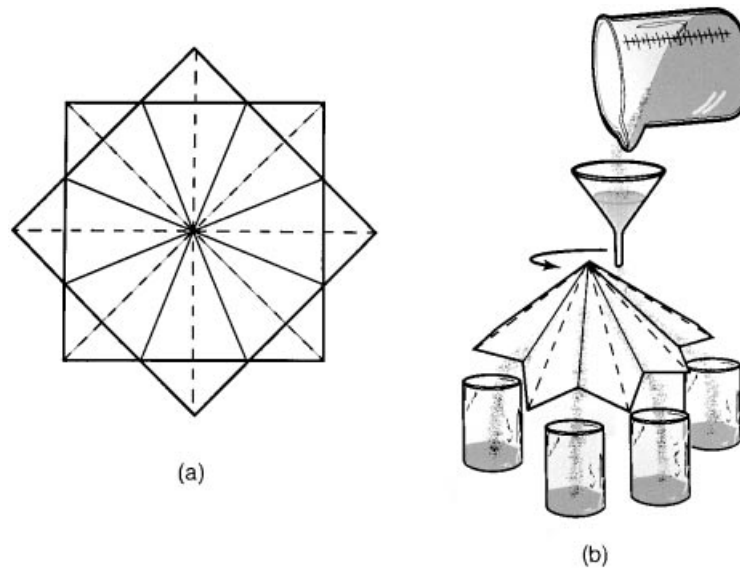
Figure 2. Paper cone riffle splitter. (a) This template for a paper cone riffle splitter is based on two 15 cm squares, one rotated 45 ° with respect to the other. (b) The sample is poured through a funnel rotated around the center of the paper cone.

The cone is centered above a ring of eight containers having 50 mm diameters. Each trough in the paper will feed a container when a powdered sample is poured onto the splitter (Figure 2(b)). The sample is poured through a hand-held funnel (VWR #30252-955) onto the paper cone in a circular motion of 50 mm diameter centered on the apex of the cone. The sample material is dropped from a height of no more than 20 cm to avoid sample loss. At least 20 rotations must be completed before the contents of the funnel are dispensed, using a uniform rotational speed. Each of the containers will now contain one-eighth of the original sample amount.

For this study an 80 g sample was split into 10 g aliquots in the first pass. One of the containers was randomly selected to undergo a second pass. After the second pass, each container contains 1·25 g. Four of the eight containers were randomly

selected and combined to give 5 g of analytical sample. For exhaustive analyses, all containers from the first pass underwent a second pass. Four containers from each second pass were randomly selected and combined to give the analytical sample, for a total of 16 5 g subsamples. The time required to generated the first subsample was about 2 min.

Fractional shoveling involves taking a series of small scoops (or shovelfuls) of sample and placing them in a series of smaller piles (Figure 3). The number of piles is determined by the sample size requirements. Individual scoops are placed on each pile in succession, repeating until the original pile is completely distributed. The number of scoops per pile ranges from 10 to 30 or more.

Fractional shoveling was performed on samples contained in secondary glass jars instead of loose piles on a sheet of paper. Measurable losses were encountered using piles on
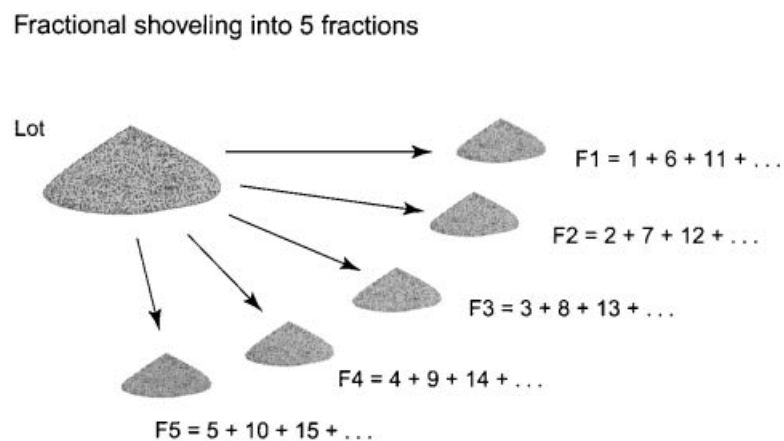
Fractional shoveling into 5 fractions

Figure 3. Fractional shoveling systematically apportions the original sample into a number of subsamples, one scoop at a time.
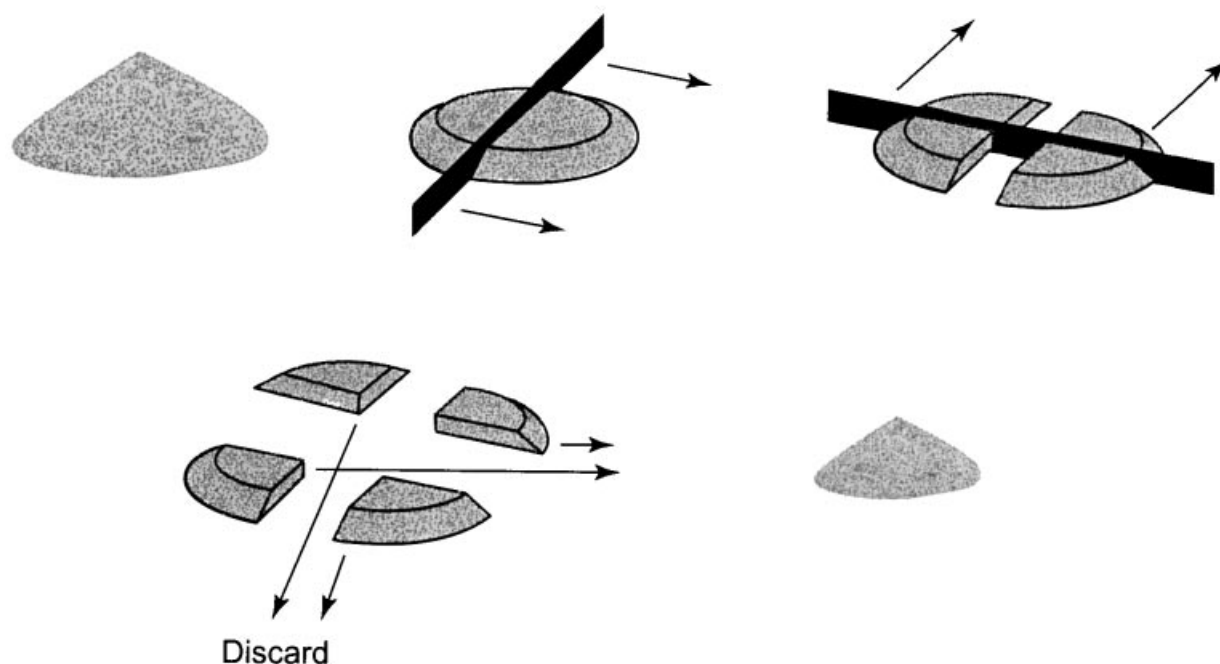
Coning & quartering

Discard

Figure 4. Coning and quartering repeatedly divides a sample into halves until the desired sample size is achieved.

paper, as some sample was scattered during recovery processes. The loose pile approach also increases exposure of the analyst to the sample and promotes contamination. A 0·7 ml measuring scoop, delivering ~1 g per scoop, was used to obtain each sample aliquot from the primary pile. A 0·3 ml measuring scoop, delivering ~0·5 g per scoop, was used to obtain the sample aliquots from the secondary piles. Scoops were taken using the method described for grab samples. For an 80 g sample the primary pile delivers 20 scoops to each secondary pile, and the secondary piles deliver about 10 scoops to each of 16 5 g piles. Reducing the mass to 5 g aliquots takes about 8 min, with notable improvement with practice. This method is applicable to moist, sticky samples as well as dry, free-flowing materials.

Coning and quartering begins by arranging the sample into a pile, flattening the pile and dividing it into quadrants (Figure 4). In this study a test sample was carefully poured into a cone on a piece of paper on a flat surface. A thin, flat piece of cardboard was driven through the apex of the pile and dragged perpendicular for a few centimeters to divide the pile in half. The cardboard was then lifted and rotated 90° and driven through the center of the separated piles. By dragging the cardboard another few centimeters in a perpendicular direction, four piles were generated.

Opposing quarters were combined, and coned and quartered in the same manner, each time saving the rejected piles for further quartering. Quarter selection for combining was always the first and third quadrants, starting in the upper right in a clockwise direction. The second and fourth quadrants were always saved for later coning and quartering. After four passes, 16 5 g samples were available for analysis in approximately 5 min.

Grab sampling consists of taking a sample using a scoop or spatula by simply inserting the sampling device into the sample container and removing an aliquot. Grab sampling is not recommended as a subsampling technique as it fails to meet the Gy sampling criterion that each part of the sample must have an equal probability of being selected [1]. This technique was included because it is commonly used despite previous studies showing its poor performance.

For grab sampling, a 3·4 ml measuring scoop with a nominal 5 g capacity was used to remove each subsample from an unstirred sample. The scoop is placed just off-center above the sample and pushed to the approximate center of the sample mass in a parabolic motion, then out of the sample. The extracted material is leveled by tapping the scoop on the side of the container to dislodge extra material. Although some mixing of the layers occurs while scooping, the initial scoops are expected to be enriched with lower-density analytes or analytes in the upper layers of the sample. There is a high probability that sampling errors will occur and accuracy should be poor with unmixed layered samples. A layer on the bottom of the jar may be entirely missed. In practice, grab sampling uses no more than the first few scoops for an analysis. Consequently, when determining the merits of grab sampling, the emphasis is on results from the initial scoops. Advantages of grab sampling include minimal exposure of the analyst to the sample, minimization of contamination, and speed (<1 min per sample), and there are no special equipment requirements.

Test samples were prepared in 4 oz glass jars. Each sample was composed of three components: sand, NaCl and magnetite. The NaCl and magnetite were present at

Table I. Layer patterns for each block in the experimental design

Position	Block 1	Block 2	Block 3
1 (top)	Magnetite	NaCl	Sand
2	Sand	Sand	NaCl
3	NaCl	Magnetite	Sand
4 (bottom)	Sand	Sand	Magnetite

approximately 6·25% (w/w) and are the analytes in this study. The sample splitting procedures could be influenced by particle size and density. The bulk of the test samples consisted of either fine- or coarse-grained screened sand. Fine grain sand had particle sizes between 0·053 and 0·150 mm and coarse grain particles ranged from 0·212 to 0·250 mm in diameter. Fine grain sand was used in half of the samples and coarse grain sand was used in the other half.

Each sample consisted of four layers: two sand, one NaCl and one magnetite. The two sand layers contained 35 g each and always separated the critical content layers. Critical content layers were always 5 g of NaCl ($\delta = 2\cdot165 \text{ g cm}^{-3}$) or 5 g of magnetite ($\delta = 5\cdot175 \text{ g cm}^{-3}$). Critical content particle sizes were coarse (0·250–0·212 mm diameter). Thus all the components were very similar in terms of particle size and shape. The experimental design included three factors: (1) subsampling method, (2) block (layer) pattern (Table I) and (3) grain size of sand. There were five methods, three blocks and two grain sizes, or 30 sample containers.

Fundamental error estimates from Gy sampling theory were calculated using the following approximation from Reference [7]:

$$\sigma_{\text{FE}}^2 = \left(\frac{1}{M_S} - \frac{1}{M_L} \right) d^3 fgcl \tag{1}$$

where σ_{FE} is the fundamental error expressed as a relative standard deviation, M_S is the mass of the aliquot or subsample (in g), M_L is the mass of the original sample (in g), d is the upper 95th percentile of the linear dimension for all particles (in cm), f is a shape factor, g is a granulometric factor, c is a mineralogical factor (g cm^{-3}) and l is a liberation factor. For the particle characteristics of the above samples, parameter estimates followed the assignments listed by Smith [7]: $f = 1$, $g = 0\cdot55$, $l = 1$ and $c = \delta/p_w$, where p_w is the weight proportion of the analyte (0·065 for either analyte) and δ is the density of the analyte. The resulting fundamental error estimates for salt and magnetite are 0·7% and 1·0% relative standard deviation (RSD) respectively. These estimates apply to all subsampling methods, as the fundamental error is based on the physical characteristics of the sample and is unrelated to the sampling method.

2.1 Analytical methods

Conductivity was used to determine NaCl, and magnetic separation and gravimetric analysis were used to determine magnetite. Each 5 g aliquot was weighed and placed on a sheet of paper. The magnetite was removed with a magnet, dropped onto a clean area of the paper, recaptured with the magnet and weighed on a balance to the nearest 0·001 g. The

Table II. Bias results (in %) from quadruplicate analysis

Grain	Block	Component	Method				
			1	2	3	4	5
Fine	1	NaCl	15·38	−1·06	4·99	−2·03	16·89
		Magnetite	−2·76	−0·26	−6·02	2·92	12·81
		Sand	−0·85	0·09	0·08	−0·06	−2·14
	2	NaCl	−12·48	4·40	−10·87	2·34	36·68
		Magnetite	−5·43	−3·55	−1·56	14·49	−3·94
		Sand	1·28	−0·06	0·89	−1·20	−2·35
	3	NaCl	2·85	−0·38	−0·94	1·50	7·80
		Magnetite	−2·09	−8·87	−2·76	3·34	−60·02
		Sand	−0·05	0·66	0·26	−0·35	3·75
Coarse	1	NaCl	−2·62	−4·89	−4·71	−5·01	32·40
		Magnetite	−7·74	−0·53	4·01	20·14	14·47
		Sand	0·74	0·39	0·05	−1·53	−3·47
	2	NaCl	−5·76	0·45	−8·58	0·20	19·48
		Magnetite	−1·05	0·59	−1·65	−0·94	22·60
		Sand	0·49	−0·07	0·73	0·05	−3·01
	3	NaCl	−5·28	−10·66	−5·91	−12·09	7·85
		Magnetite	8·42	−4·30	19·80	17·62	−75·20
		Sand	−0·22	1·07	−1·00	−0·39	4·81

Block 1 = magnetite, sand, NaCl, sand.
Block 2 = NaCl, sand, magnetite, sand.
Block 3 = sand, NaCl, sand, magnetite.
Method 1 = riffle splitter.
Method 2 = paper cone riffle splitter.
Method 3 = fractional shoveling.
Method 4 = coning and quartering.
Method 5 = grab sampling.

Table III. Precision results (in %) from quadruplicate analysis (3 × RSDs)

Grain	Block	Component	Method 1	Method 2	Method 3	Method 4	Method 5
Fine	1	NaCl	16·26	8·03	25·53	53·07	101·21
		Magnetite	12·25	12·18	16·22	39·75	78·83
		Sand	1·73	1·30	2·80	2·87	9·33
	2	NaCl	23·64	10·55	20·51	46·18	111·61
		Magnetite	18·88	11·13	26·58	24·33	142·78
		Sand	1·21	1·14	3·00	4·46	6·90
	3	NaCl	31·95	18·03	29·32	65·50	40·06
		Magnetite	20·88	34·59	14·49	26·22	189·16
		Sand	1·96	2·29	1·58	6·06	7·13
Coarse	1	NaCl	6·71	31·89	77·73	25·41	82·46
		Magnetite	9·38	8·05	21·90	20·18	101·37
		Sand	0·70	2·09	5·41	2·15	6·60
	2	NaCl	8·12	21·59	32·80	106·72	156·87
		Magnetite	15·01	8·70	14·62	18·70	64·43
		Sand	1·20	1·84	3·04	8·73	9·18
	3	NaCl	8·82	35·64	74·81	23·14	89·02
		Magnetite	15·23	28·68	16·86	17·72	344·94
		Sand	0·76	2·87	6·29	1·18	9·97

RSD: relative standard deviation.
Block 1 = magnetite, sand, NaCl, sand.
Block 2 = NaCl, sand, magnetite, sand.
Block 3 = sand, NaCl, sand, magnetite.
Method 1 = riffle splitter.
Method 2 = paper cone riffle splitter.
Method 3 = fractional shoveling.
Method 4 = coning and quartering.
Method 5 = grab sampling.

secondary drop and pick-up step eliminates sand and NaCl particles trapped with the initial magnetite pick-up.

The remaining sand/NaCl mixture was then transferred into a 50 ml plastic centrifuge tube and 35·00 ml of deionized water was added. After capping and mixing, the sample was analyzed for NaCl using a conductivity probe, with an accuracy of 0·002 g. The amount of sand was calculated by difference. Relative to exhaustive analysis, analytical bias was no more than 1% and analytical imprecision no more than 0·2% RSD. Extensive details of the experimental design and analytical results are contained in Lockheed Martin Report LM-GSA-40-14, June 30, 2000, prepared for the US EPA, Las Vegas, NV.

3.   RESULTS

The first four subsamples from each container were analyzed, providing 120 sets of results. Results are summarized in terms of bias (Table II) and precision (Table III) for each component. Statistical assessment utilized an analysis of variance (ANOVA) calculated with SAS [8] as a Type III model, using main and cross terms.

The statistical analysis is designed to identify whether the mean results from all subgroups of data are homogeneous. Thus, if a sample splitting method is found to be statistically significant, then that suggests that at least one method results in significantly different average results compared with the other methods. Summary statistics from the ANOVA show that the sample splitting method is statisti-

cally significant for both magnetite and NaCl (Table IV). The block pattern and the method*block interaction term were statistically important for both sand and magnetite. Whether the sand grain size was fine or coarse had little effect, and cross terms including grain size were also unrelated to performance.

Interestingly, there is a statistical effect based on the block. In the experimental design, there are two block patterns with sand at layers 2 and 4 and one block pattern with sand at layers 1 and 3. This resulted in a statistically significant difference related to the mean amount of sand. The cause can be traced to sampling of block 3 (Table V). The design included two block patterns with sand at the bottom and only one block pattern (#3) with sand only in the upper

Table IV. ANOVA results

Term	DF[a]	Sample constituents NaCl (%) Prob >F	Magnetite (%) Prob >F	Sand (%) Prob >F
Method	4	**0·0006**	**0·0001**	0·1760
Block	2	0·4773	**0·0004**	**0·0003**
Grain	1	0·2660	0·0744	0·7852
Method*block	8	0·6932	**0·0001**	**0·0001**
Method*grain	4	0·9946	0·9390	0·9542
Block*grain	2	0·8744	0·8903	0·9685

[a] Degrees of freedom.

Table V. Average percentage recovery for each analyte by individual factor type

Factor	Individual type	NaCl (%)	Magnetite (%)	Sand (%)
Method	Riffle splitter	6·12	6·10	87·8
	Paper cone riffle splitter	6·13	6·08	87·8
	Fractional shoveling	5·99	6·39	87·6
	Coning and quartering	6·11	6·87	87·0
	Grab sampling	**7·53**	**5·33**	87·1
Block	Magnetite/sand/NaCl/sand	6·53	6·48	87·0
	NaCl/sand/magnetite/sand	6·43	6·37	87·2
	Sand/NaCl/sand/magnetite	**6·17**	**5·61**	**88·2**
Grain	Fine	6·52	5·98	87·5
	Coarse	6·24	6·33	87·4

layers. The result was a small bias toward higher levels of sand. The method*block cross term is most likely an artifact from the block effect. The results for magnetite and NaCl show that the most important effect for analytes is the subsampling method.

While grab sampling is the easiest and fastest subsampling procedure to perform (<1 min), it is most affected by initial sample mixing. Grab sampling preferentially favors the upper layers, while riffle splitting produced more uniform uncertainty for each analyte (Table V). The difference between magnetite and NaCl is that magnetite also showed a block effect. This effect may be due to the fact that only three block patterns were studied. Magnetite occupied levels 1, 3 and 4 while NaCl occupied levels 1, 2 and 3 respectively

for the individual block patterns (Table I). Magnetite, owing to its high density, tends to settle into the lower levels as the sample is processed. The significant block and method*block ANOVA terms strongly suggest that the extent of this settling depends upon process details and where the magnetite layers are in the block design. The low mean recovery for block pattern 3, where magnetite is the bottom layer, supports this explanation.

A summary of performance by sample splitting technique is given in Table VI. Precision values are shown as $3 \times$ RSDs, which approximate a 99% confidence limit. Riffle splitting has the smallest bias (less than 2%) and the best precision (15%–16% for each analyte). The paper cone riffle splitter was second overall, followed by fractional shoveling, coning and quartering, and finally grab sampling. Owing to the layered samples, grab sampling performed very poorly. Analyte precision ranged from 97% to 154% for this technique.

Precision results are summarized in Table VII with respect to method characteristics related to Gy sampling theory. All methods had much higher variability than the fundamental error estimated with Gy sampling theory. This was expected owing to the initial layered conditions in the samples that enhance error due to grouping and segregation effects. Given these conditions and the fact that many parameter values in Equation (1) are approximations, it is remarkable that the precision for riffle splitting was only a factor of five larger than the fundamental error estimate.

The number of increments involved in each step and the fraction of the sample forwarded to the next step are shown in the right half of Table VII for each method. In addition, the last column provides a qualitative assessment of the

Table VI. Performance characteristics by sample splitting method

	Riffle splitter	Paper cone riffle splitter	Fractional shoveling	Coning and quartering	Grab sampling
Bias (%)					
NaCl	−1·3	−2·0	−4·3	−2·5	20·2
Magnetite	−1·8	−2·8	2·0	9·6	−14·9
Sand	0·2	0·3	0·2	−0·6	−0·4
Precision[a] (%)					
NaCl	15·9	21·0	43·5	53·3	96·9
Magnetite	15·3	17·2	18·4	24·5	153·6
Sand	1·3	1·9	3·7	4·2	8·2

[a] Precision levels are given as $3 \times$ RSDs.

Table VII. Precision versus sample splitting process characteristics

Method	Rank	Precision (RSD, %)			Increments for the step, fraction retained				Increment correlation
		NaCl	Magnetite	Sand	Step 1	Step 2	Step 3	Step 4	
Riffle splitter	1	5·3	5·1	0·4	12, 1/2	12, 1/2	12, 1/2	12, 1/2	Low
Paper cone riffle splitter	2	7·0	5·7	0·6	8, 1/8	8, 1/2	—	—	Low
Fractional shoveling	3	14·5	6·1	1·2	80, 1/4	40, 1/4	—	—	High
Coning and quartering	4	17·8	8·2	1·4	4, 1/2	4, 1/2	4, 1/2	4, 1/2	High
Grab sampling	5	32·3	51·2	2·7	1, 1/16	—	—	—	High
Fundamental error	—	0·7	1·0	—	—	—	—	—	—
Chemical analysis	—	0·13	0·19	—	—	—	—	—	—

RSD: relative standard deviation.

probability that particles correlated by location will be contained in the subsample. It is difficult to quantify each method's effect on the grouping and segregation error. For example, pouring the sample into the paper cone riffle splitter reduces the chance that adjacent particles will be selected for analysis. The grouping and segregation error is reduced by sampling the stream of particles in small time increments as one pours the sample around the paper cone. This produces a very large, but unknown, number of increments and a reduced grouping and segregation error. The increment correlation ranking in Table VII is only low or high, reflecting the difficulty in quantifying this effect. A low value means that spatially correlated particles are less likely to be simultaneously selected for analysis.

For the fractional shoveling method the number of increments appears very large. However, the variability is controlled by the weakest step in the method. In this case it is the 80 1 g portions in the first stage. Only 20 1 g scoops are passed to the second stage. Since each scoop removes spatially correlated particles, fractional shoveling has difficulty giving every particle an independent chance of being selected, and it tends to preserve uncertainty from grouping and segregation error. This is why the variability for fractional shoveling is similar to the variability for coning and quartering rather than riffle splitting.

The number of increments, their size and the way they are generated influence the variability in the reported results. It is evident from Table VII that method performance is best with high numbers of increments combined with a low probability that the subsample contains particles spatially correlated in the original sample. For the sample types used in this study, the number of increments is less important than the conditional probability that a particle will be selected given that an adjacent particle was selected.

4. CONCLUSIONS

For dry flowable samples a riffle splitter produced the smallest overall inaccuracy levels. The non-traditional paper cone riffle splitter provided results that were only slightly less accurate. A ceramic or plastic version of the paper cone riffle splitter could make this simple device easier to use and might produce even better results. Accuracy for fractional shoveling and coning and quartering methods were intermediate in performance. Coning and quartering resulted in higher variability than fractional shoveling and was more biased for the initial sample splits.

The study confirms that grab sampling is a poor method for subsampling particulate samples. While preliminary mixing may reduce some of the large uncertainty associated with grab sampling, it is very difficult to overcome naturally occurring heterogeneity factors such as density effects. In many cases these effects are not reduced by preliminary stirring or mixing. The conclusion that grab sampling should be avoided supports the recommendations from similar studies of this method[5,9]. Likewise, coning and quartering cannot be recommended, as alternative methods easily outperformed it. This conclusion supports Pitard's [2] recommendation to avoid coning and quartering.

The imprecision was large relative to the bias for all

methods. Thus, for a single analysis, bias is of secondary importance, since random error will have more of an effect in determining the reported value. Performance was in general agreement with the rank order one might expect based on Gy sampling theory, and was related to the number of increments, the amount of mixing and, ultimately, the chance that any set of particles might be selected for analysis.

While an equal probability that any particle will be sampled is a requirement for correct sampling in Gy theory, it is not sufficient to determine a method's performance. The conditional sampling probability for adjacent particles is directly related to the amount of grouping and segregation error retained by the sampling methodology, and this factor must be minimized if the uncertainty of a method is going to be close to the fundamental error.

The study results also demonstrate that inaccuracy associated with sample splitting can easily overwhelm inaccuracy introduced by field or laboratory analytical methods. Producing results of appropriate quality for decisions concerning hazardous waste sites requires an evaluation of the sampling and subsampling inaccuracy. These rarely characterized sources of uncertainty should not be ignored, as they can be the dominant source of error for the laboratory analysis of soils.

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