

Tested Demonstrations

A Classroom Exercise in Sampling Technique

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It is important for students to appreciate the challenge of obtaining an analytical sample representative of the bulk material. The first step in any chemical analysis is to obtain such a sample. In fact, the sampling determines the overall analytical result. The sample must be representative of the material to be analyzed, or the remaining analysis, regardless of precision, is meaningless. Other than a brief introduction, introductory analytical texts give little attention to problems encountered in obtaining such a sample. This is partly because of the amount of background information needed by the student and the time involved in presenting the subject well. Though this trivializes the sampling process, leaving the students to believe a priori that sampling is a problem, they still must face this problem directly.

Kratovich published an excellent experiment in this *Journal* that attempted to get at the heart of the sampling process, looking at particle size, sample size, and sample composition (1). The experiment used the analysis of potassium hydrogen phthalate, which can be done with high precision by an experienced analyst, to illustrate to the student the importance of the sampling step. Cohen, in his articles in this *Journal*, presents an argument for the random sample, which if taken correctly and in sufficient numbers can well represent the population from which it is drawn (2, 3). All these articles present the difficulty and issues in the process very well, but one experiment requires an extended laboratory period, and the other articles are very theoretical.

For the past four years, students in my class have been using a classroom exercise demonstrating the effect of sample size and particle size. The exercise uses readily available materials with no disposal problems and the data can be obtained easily within a 45-minute class period.

Sample Size

To look at sample size one needs to have an easy means of developing different sized samples that are relatively consistent in the amount of sample taken each time.

This exercise is set in the context of being approached by a competitor candy manufacturer looking for the color composition of M&M candy. M&M/Mars¹ produces M&M's in packages of a variety of sizes, which can be purchased in any supermarket. In the exercise, bags of M&M's are handed out to small groups of students (3–4 students per group). Three sizes of bags, 0.8 oz (available in a Halloween Pac), 10

oz, and 16 oz, are used. Enough bags of each size are distributed so that the data can be analyzed statistically and the total number of pieces from bags of each size is approximately the same. Each group opens their bag or bags, counts the total number of candies, and reports the percentage of candy pieces of each color. Table 1 gives results from a typical classroom exercise where only three colors of M&M's are counted and reported. All colors are included in the total pieces in each bag.

The raw data are compiled at the end of the period and the students are asked to analyze the results, *Q*-testing apparent outliers (4) within a sample type and testing for significant differences between the three sample sizes. Data have been accumulated for the past four years, with results similar to those given in the table. The current students are given the accumulated data, by year, and asked to determine any difference from one year to the next. Using pooled standard deviations to test for significant differences, they easily see that as the sample size increases, the variance in the data decreases. As a reward, they are able to take the M&M's with them as a snack.

Table 1. Sample Size, M&M Candies

Sample Type	Total Pieces per Bag	% Pieces of Color:		
		Red	Yellow	Blue
0.8-oz bag	22	23	5	0
	23	22	21	9
	23	13	30	30
	23	17	22	9
	23	17	13	17
	Mean ^a	18.3	15.6	13.6
10-oz bag	SD ^a	6.3	8.0	8.2
	331	23	17	14
	333	22	19	11
	333	22	20	11
	334	22	18	12
	336	25	23	10
16-oz bag	Mean	22.8	19.4	11.6
	SD	1.3	2.3	1.5
	513	28	30	10
	514	27	28	8
	522	28	25	9
	Mean	27.6	27.6	9.0
	SD	0.5	2.5	1.0

^aCalculated from data of whole class, not from the partial data shown.

Particle Size and Non-homogeneous Samples

Investigating the effects of variation in particle size on the ability to take a "grab" sample representing the composition of the whole requires a material whose particle size varies in a regular way. The material must also be easy to separate and analyze by particle size.

To address the particle size concern, students have used NERDS, a product of the Willy Wonka Candy Factory,² for the past three years. NERDS are packaged in boxes containing two different flavors. The grape-flavored candies are much larger "particles" than the other flavors. In the first year it was necessary to go to several different stores to get enough boxes of the same two flavors to have samples for each student. The second year, the Willy Wonka Candy Factory donated two slightly different-sized flavors, grape (purple) and watermelon (pink), in bulk. The factory also included a small amount of their starting sugar (white), which is a fairly large crystalline material although the particles are much smaller than NERDS particles of either flavor.

Representative samples of the same known composition were prepared to provide each group of students with their own sample in a plastic bag. The students were then given a small (10-mL) beaker as their sampling device and asked to take five aliquots of their laboratory sample. By counting the number of each type of candy, a composition for the sample was obtained. Table 2 shows typical results for this sampling exercise.

The data clearly show that an inhomogeneous sample is extremely difficult to sample, the larger particles giving much more consistent results with smaller variance than the smaller particles as a consequence of segregation within the sample. The students can see that even the same person, taking multiple samples, cannot obtain accurately reproducible results. The data are compiled and students determine if there is a significant difference between the laboratory samples provided, considering the variability of the results, and they compare their results with the known composition. They also calculate the variance for each size of particle and see the difference in variance between the large and small particles.

These exercises show quite vividly the problems associated with taking a representative sample of a bulk material. They make the discussion presented in the text more "real". They also tell the student that sampling is a real problem, which they will encounter when they begin to analyze real-world products. These exercises create a better balance between the importance of sampling and the other material covered in a typical text.

Table 2. Particle Size, NERDS Candies

Group	Trial	No. of Pieces in Aliquot	% Pieces of Color:		
			Purple	Pink	White
I	1	81	59	41	0
	2	98	53	34	13
	3	155	55	21	24
	4	164	48	22	30
	5	185	52	15	33
	Mean		53	27	20
	SD		4	11	14
II	1	147	46	20	24
	2	186	46	27	34
	3	224	41	22	37
	4	252	39	10	48
	5	371	34	13	48
	Mean		41	18	38
	SD		5	7	10
III	1	173	53	24	24
	2	223	47	7	46
	3	226	52	9	39
	4	283	53	8	30
	5	296	58	8	24
	Mean		53	13	33
	SD		4	7	10

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Notes

1. M&M/Mars, Division of Mars, Inc., Hackettstown, NJ 07840.
2. Willy Wonka Candy Factory, 1445 West Norwood Ave., Itasca, IL 60143.

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