Accounting for Mixture Errors in Analyzing Mixture Experiments

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Until now, mixture errors that cause the actual mixture proportions to differ from those intended have not been considered in the analysis of mixture experiments. In this article, we show how a Bayesian approach can account for such errors. A simulation study shows the problems with ignoring these errors and also the benefits of accounting for them. The proposed approach is illustrated with a semirealistic glass mixture experiment.

KEY WORDS: Bayesian Method; Error-in-Variables; MCMC.

Introduction

MANY products are made by mixing various components. Paint, plastic, bread and fruit drinks are good examples. For such products, it is of interest to determine what component proportions lead to desirable results in terms of quality characteristics such as yield or texture. Let x_j, $j = 1, \ldots, q$, represent the proportions of q components, where $\sum_{j=1}^{q} x_j = 1$, and let y represent the quality characteristic of interest. In this case, due to the constraint on the proportions, the feasible region of mixtures is a simplex (e.g. a triangle for three components).

Mixture experiments, consisting of sets (runs) of component proportions, allow one to develop a model for the response y in terms of the component proportions. Scheffé (1958) developed canonical polynomials of various orders to model the mixture response. His first-degree model takes the form

$$y = \sum_{j=1}^{q} \beta_j x_j + \epsilon, \tag{1}$$

where the x_j are the mixture proportions, the β_j are the linear blending coefficients and the error term ϵ is assumed to be $N(0, \sigma^2)$ and independent of the mixture proportions. Note that the model in Equation (1) does not contain an intercept term β_0 because of the constraint $\sum_{j=1}^{q} x_j = 1$. Scheffé's second-degree model takes the form

$$y = \sum_{j=1}^{q} \beta_j x_j + \sum_{1 \le k < l \le q} \beta_{kl} x_k x_l + \epsilon. \tag{2}$$

See Cornell (2002) for more information regarding such models and mixture experiments in general.

Until now, errors in the mixture proportions have not been considered in the analysis of mixture experiments. Steiner and Hamada (1997) studied the impact of mixture errors about an intended set of proportions on the resulting response. They found that the variance is larger than σ^2 because of the transmission of the mixture errors through the expectation (i.e., $\sum_{j=1}^{q} \beta_j x_j$) of the mixture response model in Equation (1).

Let us consider a simple example with $q = 3$ to see the difficulties in accounting for mixture errors in

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the analysis. Suppose that the intended set of proportions is $(0.25, 0.50, 0.25)$ and that this is achieved by mixing the amounts $(25, 50, 25)$ in liters. Note that, even if only one amount is off, say 24 liters for the first component instead of 25 liters, then the actual set of proportions is $(24/99, 50/99, 25/99) = (0.242, 0.505, 0.253)$ and none of the intended proportions are achieved. Even if the errors in the component amounts are independent, the errors in the component proportions are still dependent.

In this article, we show how a Bayesian approach can account for mixture errors in the analysis of mixture experiments that is easily implemented in commonly available software. The benefit is that σ^2 is no longer overestimated, which impacts the inference on the model coefficients (β's) and prediction intervals.

An outline of this article is as follows. First, we discuss mixture errors and present a Bayesian approach that accounts for them. Through a simulation study, we show the impact of ignoring mixture errors in the analysis of mixture experiments and the benefits of the Bayesian approach. Then we consider a semirealistic example, a glass mixture experiment, to illustrate the Bayesian approach. Next, we discuss modeling and assessing mixture errors. Finally, we end with some conclusions.

A Bayesian Approach for Handling Mixture Errors

We begin by considering absolute mixture errors, which can be described by

$$a_j = x_j \times \mathrm{A} + \delta_j, \tag{3}$$

where $\delta_j \sim N(0, \sigma^2_{\mathrm{mix},j})$. That is, for a mixture for which the target total amount for all components is A, $x_j \times \mathrm{A}$ is the intended amount for the jth component, and a_j is the actual amount with additive error δ_j.

The actual proportion is

$$z_j = \frac{a_j}{\sum_{k=1}^{q} a_k}, \tag{4}$$

which will be different from the intended proportion x_j. We assume that the $\sigma^2_{\mathrm{mix},j}$ are known. If unknown, they can be quantified as discussed in a later section.

For a mixture experiment in n runs with mixture errors, assume the ith response y_i follows

$$y_i = \sum_{j=1}^{q} \beta_j z_{ij} + \epsilon_i, \tag{5}$$

where z_{ij}, $j = 1, \ldots, q$ are the actual proportions and $\epsilon_i \sim N(0, \sigma^2)$. Note that the responses depend on the actual proportions, which are unknown. We assume a first-degree mixture model, but the Bayesian approach also handles second-degree and other mixture model forms.

Next we consider a Bayesian approach that handles mixture errors. Bayesian inference provides uncertainty in the unknown quantities $\boldsymbol{\theta} = (\beta_j,\ j = 1, \ldots, q;\ \sigma^2;\ z_{ij},\ i = 1, \ldots, n,\ j = 1, \ldots, q)$ through the joint posterior distribution. It does so by combining prior information about $\boldsymbol{\theta}$ with the information about $\boldsymbol{\theta}$ contained in the response data $\mathbf{y} = (y_i, \ldots, y_n)$. The prior information is described by a probability density, $\pi(\boldsymbol{\theta})$, known as the prior density and the information provided by the data is captured by the data sampling model, $f(\mathbf{y} \mid \boldsymbol{\theta})$, known as the likelihood. The combined information is then described by another probability density, $\pi(\boldsymbol{\theta} \mid \mathbf{y})$, called the joint posterior density. Bayes' Theorem provides the way to calculate the joint posterior density, namely,

$$\pi(\boldsymbol{\theta} \mid \mathbf{y}) \propto f(\mathbf{y} \mid \boldsymbol{\theta})\pi(\boldsymbol{\theta}).$$

Because the data are assumed to be independent and normally distributed, the data sampling model or likelihood is the product of n Gaussian densities as defined by Equation (5) and evaluated at the observed data values, $y_1, \ldots, y_n$. Any available knowledge regarding reasonable ranges of values for the β_j and σ^2 may be incorporated in priors for them. Otherwise, diffuse priors might be used, such as

$$\beta_i \sim N(0, 10^6), \quad \sigma^2 \sim IG(10^{-6},\ 10^{-6}), \tag{6}$$

where IG denotes the inverse gamma distribution. No priors for the z_{ij} are required because their distribution is specified by Equations (3) and (4).

Markov chain Monte Carlo (MCMC) (Gilks, Richardson, and Spiegelhalter (1996)), such as Gibbs sampling (Casella and George (1992)), can be used to obtain simulated draws from the joint posterior distribution. The marginal posterior of each of $(\beta_j,\ j = 1, \ldots, q;\ \sigma^2)$ can then be used to make inferences about these parameters of interest. Gibbs sampling consists of repeated cycles of draws from the full conditional distributions, where the full conditional distributions for the mixing experiment are β_1

given ($\beta_k, k \neq 1$, σ^2, z_{ij}, $i = 1, \ldots, n$, $j = 1, \ldots, q$), ..., β_q given ($\beta_k, k \neq q$, σ^2, z_{ij}, $i = 1, \ldots, n$, $j = 1, \ldots, q$), σ^2 given (β_k, $k = 1, \ldots, q$, z_{ij}, $i = 1, \ldots, n$, $j = 1, \ldots, q$), and $z_{1,1}$ given (β_k, $k = 1, \ldots, q$, σ^2, z_{ij}, $i = 1, \ldots, n$, $j = 1, \ldots, q$, $i \neq 1$ and $j \neq 1$), ..., and $z_{n,q}$ given (β_k, $k = 1, \ldots, q$, σ^2, z_{ij}, $i = 1, \ldots, n$, $j = 1, \ldots, q$, $i \neq n$ and $j \neq q$). In the preceding sentence, "given" means that the remaining parameters are set at their current values. The density of the full conditional distribution for a specified parameter is identified up to a constant by collecting all the terms in the joint posterior density, i.e., the product of the likelihood and prior densities, that involve that parameter. In simple cases, the full conditional distributions turn out be well-known distributions that are easily sampled. In more complicated situations, such as for mixture experiments with mixture errors, the full conditional distributions can still be sampled using the Metropolis–Hastings algorithm (Chib and Greenberg (1995)). Fortunately, the practitioner does not have to worry about all these details because WinBUGS (Gilks et al. (1994)) can easily implement MCMC, as will be shown later in the example.

Simulation Study

We performed a simulation study to investigate ordinary least squares (OLS) estimates (which ignore the mixture errors) and Bayesian posterior means (which account for the mixture errors). The experimental design used was a 10-point augmented simplex centroid design as given in Table 1 for a three-component mixture. The response model assumed is the following Scheffé second-degree model (as in Equation (2), which includes all the two-component blending terms:

$$y_i = \beta_1 z_{i1} + \beta_2 z_{i2} + \beta_3 z_{i3} + \beta_{12} z_{i1} z_{i2} + \beta_{13} z_{i1} z_{i3} + \beta_{23} z_{i2} z_{i3} + \epsilon_i, \quad (7)$$

where $\epsilon_i \sim N(0, \sigma^2)$. For mixture errors, we used the absolute mixture errors described by Equation (3), with $\sigma_{\text{mix},j}$ the same for $j = 1$, 2, and 3 and having the common value of 7.5, 15, 30, and 60. The target total amount for all components was A = 1,000. Note that 7.5 is about 2.25% of the intended component amount when $x_j = 0.333333$; 15, 30, and 60 correspond to 4.5, 9, and 18%, respectively. Finally, note that there is no mixture error when x_j=0.

For the simulation study, the mixture experiment was simulated 1,000 times. For each simulation, the linear blending coefficients, the β_i, were drawn from $N(25, 25)$ (i.e., $(20.2, 29.8)$ are the distribution's 0.025 and 0.975 quantiles), the two-component blending coefficients, the β_{ij}, were drawn from $N(75, 25)$ (i.e., $(70.2, 79.8)$ are the distribution's 0.025 and 0.975 quantiles), and σ^2 was drawn from $InverseGamma(3, 0.01)$ (i.e., $(0.037, 0.127)$ are the distribution's 0.025 and 0.975 quantiles). These distributions were also used as the priors in the Bayesian approach. Absolute mixture errors were then added and the responses drawn as described by Equation (7).

The results from the simulation study are given in Table 2. The results for the linear blending coefficients, β_1, β_2, and β_3, are combined because the mixture experiment design given in Table 1 is symmetric with respect to the three components. Similarly, the results for the two-component blending coefficients, β_{12}, β_{13}, and β_{23}, are combined. These results include the root mean squared error (RMSE) of the estimated parameters and the average interval estimate length. For the OLS model fitting, the standard 90% confidence interval was used; for the Bayesian approach, the central 90% credible interval was used (i.e., the 0.05 and 0.95 quantiles of the marginal posterior) for each of the parameters. We also considered the prediction for a single observation at the component proportions $(0.333333, 0.333333, 0.333333)$, for which the expected value is $0.333333(\beta_1 + \beta_2 + \beta_3) + 0.333333^2(\beta_{12} + \beta_{13} + \beta_{23})$. Under the RMSE results, the Bayes/OLS column is the Bayes column divided by the OLS column. For interval estimate lengths, the ratio of Bayes and OLS interval-estimate lengths are computed first for each simulation and the average of the 1,000 ratios is reported for each parameter.

What do the simulation results suggest? Foremost, the response model error standard deviation, σ, is overestimated if mixture errors are ignored. The RMSE is about 4, 10, 20, and 50 times larger for OLS than Bayes for $\sigma_{\text{mix},j}$ = 7.5, 15, 30, 60, respectively. The OLS estimate of σ bias is 0.038, 0.119, 0.283, 0.641 at $\sigma_{\text{mix},j}$ = 7.5, 15, 30, 60, respectively. That is, not accounting for mixture errors makes the response appear to be more variable than it really is. This in turn impacts the length of the various interval estimates as seen in Table 2. Especially note that the OLS prediction intervals are much larger than the Bayes prediction intervals. This has practical implications because prediction is an important use of the analysis of a mixture experiment. For the linear blending coefficients (β_1, β_2, β_3), there is no difference between OLS and Bayes in terms of RMSE. For the two-component blending coefficients

TABLE 1. Augmented Simplex Centroid Design Used in Simulation Study

x_1	x_2	x_3
1.000000	0.000000	0.000000
0.000000	1.000000	0.000000
0.000000	0.000000	1.000000
0.666667	0.333333	0.000000
0.666667	0.000000	0.333333
0.000000	0.666667	0.333333
0.333333	0.666667	0.000000
0.333333	0.000000	0.666667
0.000000	0.333333	0.666667
0.333333	0.333334	0.333333

(β_{12}, β_{13}, β_{23}), the OLS RMSEs are somewhat larger than those for Bayes as σ_{mix} increases; the OLS prediction RMSEs are also somewhat larger. In summary, the simulation results suggest that there are tangible benefits by accounting for mixture errors.

Glass Mixture Experiment Example

The immobilization of nuclear waste is an important and challenging problem for the United States and other countries. Vitrification, which turns the waste into glass, is one technology that addresses this problem. Hrma et al. (1994) performed a composition variation study (CVS) in support of a proposed future nuclear waste vitrification plant. From 1989 to 1994, over 120 nonradioactive glasses were melted and properties measured in a series of statistically designed mixture experiments. The composition of each glass is represented by 10 components: SiO_2, B_2O_3, Na_2O, Li_2O, CaO, MgO, Fe_2O_3, Al_2O_3, ZrO_3 and others (all remaining components). Although several properties of the resulting glass were measured, we consider only viscosity. Using the CVS data, Hrma et al. (1994) empirically fit first- and second-degree mixture models for $\log_e$(viscosity) as a function of glass composition. The models were then validated using both internal and external data.

Viscosity was measured at three to five temperatures for each glass. For each glass, these data were then fitted to a Fulcher equation from which the viscosity at the desired temperature of 1,150^{o}C was predicted. Table 3 contains the as-batched mass fraction compositions (x_j's) of all 23 CSV-I glasses along with the corresponding Fulcher-predicted viscosity (y) at 1,150°C.

Samples of all 23 CSV-I glasses were also submitted for chemical analysis to check the as-batched compositions. The chemical analysis consisted of averaging the two results from a K/Ni and a Na/Zr fusion. These analytical results were then compared with the desired as-batched glass compositions. Hrma et al. (1994) attributed the observed differences to the analyzed compositions being more variable and in some cases biased as compared with the as-batched compositions. After accounting for the analytical biases, Hrma et al. (1994) did not find significant differences between the as-analyzed and as-batched compositions. Hence, for the actual glass experiment, random mixture errors in the as-batched compositions were not an issue.

For purely illustrative purposes, we suppose that there were mixture errors in this experiment for which standard deviations (SD) in mass fractions are given in the last row of Table 3. Consequently, the results and conclusions in the remainder of this section do not reflect on the results originally obtained for the actual glass experiment by Hrma et al. (1994).

For the mixture errors, we assume that Equation (3) holds so that $x_{ij} \times$ A is the as-batched (intended) amount of the jth component in the ith glass. Because the SDs in Table 3 pertain to proportions, we assume that, for the jth component amount, $\sigma_{\text{mix},j} = \text{SD}_j \times \text{A}$. When an as-batched component mass fraction is zero (i.e., the component is not present), we simply set the corresponding SD equal to 0 in the analysis.

First, consider the results obtained using OLS to fit a first-degree mixture model (Equation (1) with $\log_e$(viscosity) as the response) to the as-batched data in Table 3. Table 4 contains a summary of the ANOVA results for the fitted model, while Table 5 contains the corresponding parameter estimates and their standard errors.

Note that there is a significant lack of fit in the first-degree mixture model. Even though first-degree mixture models fit some glass properties reasonably well, many others often have significant lack of fit. Because of the sparsity of the data, we will ignore this apparent lack of fit and proceed with a Bayesian analysis based on a first-degree mixture model. Again, this decision is appropriate only for illustrative purposes.

We now use the proposed Bayesian approach for fitting a first-degree mixture model to the data in Table 3 that accounts for mixture errors. We use

TABLE 2. Simulation Results: OLS and Bayesian Approach

	RMSE			Interval estimate length		
Parameter	OLS	Bayes	Bayes/OLS	OLS	Bayes	Bayes/OLS
			$\sigma_{\text{mix},j} = 7.5$			
$\beta_1, \beta_2, \beta_3$	3.753	3.753	1.000	0.547	0.222	0.471
$\beta_{12}, \beta_{13}, \beta_{23}$	4.013	4.005	0.998	2.422	1.531	0.747
σ	0.089	0.024	0.268	0.117	0.068	0.654
Prediction	0.074	0.062	0.833	0.667	0.304	0.533
			$\sigma_{\text{mix},j} = 15$			
$\beta_1, \beta_2, \beta_3$	3.753	3.754	1.000	1.003	0.225	0.269
$\beta_{12}, \beta_{13}, \beta_{23}$	4.088	4.049	0.991	4.442	2.479	0.678
σ	0.209	0.024	0.116	0.215	0.071	0.390
Prediction	0.135	0.094	0.698	1.222	0.382	0.314
			$\sigma_{\text{mix},j} = 30$			
$\beta_1, \beta_2, \beta_3$	3.754	3.754	1.000	1.976	0.225	0.140
$\beta_{12}, \beta_{13}, \beta_{23}$	4.378	4.206	0.961	8.747	4.405	0.626
σ	0.470	0.024	0.052	0.424	0.072	0.206
Prediction	0.274	0.179	0.652	2.407	0.551	0.279
			$\sigma_{\text{mix},j} = 60$			
$\beta_1, \beta_2, \beta_3$	3.764	3.754	0.997	4.086	0.225	0.069
$\beta_{12}, \beta_{13}, \beta_{23}$	5.550	4.779	0.861	18.090	7.296	0.505
σ	1.048	0.024	0.023	0.877	0.071	0.101
Prediction	0.632	0.415	0.657	4.978	0.844	0.207

the software package WinBUGS (Gilks, Thomas, and Spiegelhalter (1994)) that is available for free download from the Web at URL http://www.mrc-bsu.cam.ac.uk/bugs/. WinBUGS is extremely easy to learn and use and, along with a comprehensive user's manual (Spiegelhalter, Thomas, and Best (2000)), includes two volumes of worked examples. The documentation is very thorough and well written. WinBUGS implements MCMC as described earlier to sample from the joint posterior distribution of the parameters.

Table 6 gives the WinBUGS code for fitting the first-degree mixture model to the data in Table 7. One point of clarification is needed for the second parameter of the Gaussian distribution: WinBUGS uses the precision, which is the reciprocal of the variance. The absolute Gaussian mixture errors were used in this analysis, and we have taken the intended total amount of the mixture A to be 1,000. We note, however, that the results do not depend on the value of A; thus, reasonable values for A can be chosen. Note also that the diffuse prior distributions (Equation (6)) used in Table 6 have almost no effect on the results.

The output obtained by executing the WinBUGS source code in Table 6 is shown in Table 7. The results in Table 7 summarize the marginal posterior distributions of the 10 parameters and the residual error standard deviation, σ. The means, standard deviations, and quantiles in Table 7 were all calculated based on 10,000 random MCMC draws from the corresponding joint posterior distributions.

Note in Table 7 that the mean of the marginal posterior distribution of σ is 0.1483, which is roughly one half as large as the corresponding OLS-based

TABLE 3. As-Batched Mass Fraction Compositions, Predicted Viscosities (y) and Mixture Error Standard Deviations (SD) for CVS-I Glasses at 1,150°C

Glass	SiO_2	B_2O_3	Na_2O	Li_2O	CaO	MgO	Fe_2O_3	Al_2O_3	ZrO_2	Others	y
CVS1-1	0.4801	0.1142	0.1003	0.0376	0.0275	0.0363	0.0568	0.0636	0.0429	0.0407	5.78
CVS1-2	0.5500	0.0500	0.0500	0.0700	0.1000	0.0000	0.0200	0.1500	0.0000	0.0100	13.29
CVS1-3	0.4200	0.2000	0.0500	0.0700	0.0000	0.0800	0.0200	0.1400	0.0100	0.0100	2.39
CVS1-4	0.5700	0.2000	0.0900	0.0100	0.0200	0.0800	0.0200	0.0000	0.0000	0.0100	8.70
CVS1-5	0.5700	0.0500	0.0700	0.0700	0.0000	0.0000	0.1500	0.0800	0.0000	0.0100	13.24
CVS1-6	0.4400	0.2000	0.0500	0.0700	0.0000	0.0000	0.0200	0.0000	0.1200	0.1000	2.01
CVS1-7	0.5700	0.0500	0.0964	0.0100	0.1000	0.0000	0.0336	0.0000	0.1300	0.0100	72.88
CVS1-8	0.5363	0.0500	0.0837	0.0100	0.0000	0.0800	0.1500	0.0000	0.0800	0.0100	29.26
CVS1-9	0.4200	0.1962	0.0538	0.0100	0.0000	0.0800	0.1400	0.0000	0.0000	0.1000	4.06
CVS1-10	0.5700	0.0851	0.0941	0.0100	0.0000	0.0000	0.0200	0.1200	0.0000	0.1000	83.83
CVS1-11	0.4200	0.1549	0.0751	0.0100	0.1000	0.0000	0.0200	0.1400	0.0000	0.0800	14.50
CVS1-12	0.4200	0.1764	0.0736	0.0700	0.1000	0.0000	0.1500	0.0000	0.0000	0.0100	0.42
CVS1-13	0.5700	0.2000	0.1862	0.0100	0.0000	0.0000	0.0200	0.0038	0.0000	0.0100	3.31
CVS1-14	0.4200	0.2000	0.1862	0.0100	0.0000	0.0000	0.0200	0.0238	0.1300	0.0100	3.42
CVS1-15	0.5589	0.0500	0.1211	0.0700	0.0000	0.0800	0.0200	0.0000	0.0000	0.1000	2.55
CVS1-16	0.4327	0.0500	0.1873	0.0100	0.0000	0.0800	0.0858	0.1442	0.0000	0.0100	17.81
CVS1-17	0.4545	0.0500	0.1455	0.0100	0.1000	0.0000	0.1400	0.0000	0.0000	0.1000	2.23
CVS1-18	0.4214	0.0500	0.1186	0.0700	0.0200	0.0800	0.0200	0.0000	0.1300	0.0900	1.87
CVS1-19	0.4801	0.1142	0.1003	0.0376	0.0275	0.0363	0.0568	0.0636	0.0429	0.0407	5.76
CVS1-20	0.4801	0.1142	0.1003	0.0376	0.0275	0.0363	0.0568	0.0636	0.0429	0.0407	5.71
CVS1-21	0.5700	0.2000	0.0900	0.0100	0.0200	0.0800	0.0200	0.0000	0.0000	0.0100	9.36
CVS1-22	0.5363	0.0500	0.0837	0.0100	0.0000	0.0800	0.1500	0.0000	0.0800	0.0100	38.11
CVS1-23	0.5153	0.0956	0.1052	0.0375	0.0289	0.0084	0.1179	0.0456	0.0063	0.0393	5.69
SD	0.0100	0.0030	0.0060	0.0040	0.0010	0.0020	0.0010	0.0020	0.0080	0.0050	

estimate of $0.2625 = \sqrt{0.06892}$. Finally, the standard deviations of the marginal posterior distributions of the parameter estimates in Table 7 are almost all uniformly smaller than the corresponding standard errors in Table 5.

However, precisely speaking, such a comparison between OLS and Bayesian estimates cannot rigorously be made because each method has a different philosophical basis. To ensure a fair comparison between the inclusion and exclusion of mixture errors, Table 8 contains the Bayesian WinBUGS results for the same case as in Table 7 except that the mixing errors are now ignored.

By directly comparing the SD column in Tables 7 and 8, we see the effect of considering mixture errors in a Bayesian analysis. The SDs of the estimated parameters are uniformly smaller for all 10 parameters when the mixing errors are considered. In

TABLE 4. ANOVA Results for the OLS Fitted First-Degree Mixture Model

Source	DF	Sum of squares	Mean squares	F	p value
Model	9	134.2540	3.80600	55.22	<0.0001
Residual error	13	0.8960	0.06892		
Lack-of-fit	9	0.8583	0.09537	10.13	0.020
Pure error	4	0.0377	0.00942		
Total (corrected)	22	35.1500			

TABLE 5. OLS Estimates and Standard Errors for Fitted First-Degree Mixture Model

Term	LSE	SE
SiO_2	8.82	0.48
B_2O_3	−6.67	0.81
Na_2O	−11.22	1.37
Li_2O	−33.11	2.20
CaO	−4.35	1.60
MgO	−0.88	1.68
Fe_2O_3	−0.54	1.06
Al_2O_3	10.93	1.10
ZrO_2	8.44	1.22
Others	−0.52	1.41

addition, the marginal posterior mean of σ is also observed to be 47% smaller when the mixture errors are included in the analysis.

Table 9 contains the WinBUGS-produced means and SDs, as well as the 0.05 and 0.95 quantiles, of the marginal posterior predictive distributions of viscosity for all 23 CVS-I glasses for the case in which mixture errors are both included and ignored. (Note that samples from the predictive distribution of $\log_e$(viscosity) are obtained by sampling the posterior distribution of the first-degree mixture model parameters and generating $\log_e$(viscosity) values according to Equation (1); samples from the predictive distribution of viscosity are then easily obtained by exponentiating the samples from the predictive distribution of $\log_e$(viscosity).) By including mixture errors, the posterior SDs in Table 9 have been reduced an average of approximately 30%. Thus, as previously noted, accounting for mixture errors in the analysis produces more precise viscosity predictions.

Modeling and Assessing the Amount of Mixture Error

In this article, we have shown the impact of ignoring mixture error in analyzing mixture experiments for absolute mixture errors as described in Equations (3) and (4). There are a number of ramifications. First, for a specific application, what is an appropriate model for the mixture errors? Steiner and Hamada (1997) also considered relative mixture errors in which the standard deviation of the component amount depends on the intended component amount; $a_i \sim N(\mu_i, (\mu_i\delta)^2)$, with $\mu_i = x_iA$, provides

TABLE 6. WinBUGS Code for Glass Experiment

```
# (Note: "0" Variances for All 0 Mixture Components)
   Model
   {
      for(i in 1:N)
         {
          w[i]<−log(y[i])
          w[i]∼dnorm(mu[i],tau)
          mu[i]<−beta[1]∗z[i,1]+beta[2]∗z[i,2]+beta[3]∗z[i, 3]
                   +beta[4]∗z[i,4]+beta[5]∗z[i,5]
                   +beta[6]∗z[i,6]+beta[7]∗z[i,7]
                   +beta[8]∗z[i,8]+beta[9]∗z[i,9]
                   +beta[10]∗z[i,10]
          for(j in 1:10)
              {
              z[i,j]<−a[i,j]/sum(a[i,1:10])
              sigmameas[i,j]<−A∗SD[i,j]
              taumeas[i,j]<−1/(sigmameas[i,j]∗sigmameas[i,j])
              eta[i,j]<−x[i,j]∗A
              a[i,j]∼dnorm(eta[i,j],taumeas[i,j])
              }
          b[i]∼dnorm(mu[i],tau)
          c[i]<−exp(b[i])
          }
       tau∼dgamma(1.0E-6,1.0E-6)
       sigma<−1/sqrt(tau)
       sigma2<−sigma∗sigma
       for(j in 1:10)
              {
              beta[j]∼dnorm(0.0,1.0E-6)
              }
   }
Data
list(SD=structure(.Data = c(
.01,.003,.006,.004,.001,.002,.001,.002,.008,.005,
.01,.003,.006,.004,.001,1.0E-20,.001,.002,1.0E-20,.005,
.01,.003,.006,.004,1.0E-20,.002,.001,.002,.008,.005,
.01,.003,.006,.004,.001,.002,.001,1.0E-20,1.0E-20,.005,
.01,.003,.006,.004,1.0E-20,1.0E-20,.001,.002,1.0E-20,.005,
.01,.003,.006,.004,1.0E-20,1.0E-20,.001,1.0E-20,.008,.005,
.01,.003,.006,.004,.001,1.0E-20,.001,1.0E-20,.008,.005,
.01,.003,.006,.004,1.0E-20,.002,.001,1.0E-20,.008,.005,
.01,.003,.006,.004,1.0E-20,.002,.001,1.0E-20,1.0E-20,.005,
.01,.003,.006,.004,1.0E-20,1.0E-20,.001,.002,1.0E-20,.005,
.01,.003,.006,.004,.001,1.0E-20,.001,.002,1.0E-20,.005,
.01,.003,.006,.004,.001,1.0E-20,.001,1.0E-20,1.0E-20,.005,
.01,.003,.006,.004,1.0E-20,1.0E-20,.001,.002,1.0E-20,.005,
.01,.003,.006,.004,1.0E-20,1.0E-20,.001,.002,.008,.005,
.01,.003,.006,.004,1.0E-20,.002,.001,1.0E-20,1.0E-20,.005,
.01,.003,.006,.004,1.0E-20,.002,.001,.002,1.0E-20,.005,
.01,.003,.006,.004,.001,1.0E-20,.001,1.0E-20,1.0E-20,.005,
.01,.003,.006,.004,.001,.002,.001,1.0E-20,.008,.005,
.01,.003,.006,.004,.001,.002,.001,.002,.008,.005,
.01,.003,.006,.004,.001,.002,.001,.002,.008,.005,
.01,.003,.006,.004,.001,.002,.001,1.0E-20,1.0E-20,.005,
.01,.003,.006,.004,1.0E-20,.002,.001,1.0E-20,.008,.005,
.01,.003,.006,.004,.001,.002,.001,.002,.008,.005
),.Dim = c(23,10)),
N=23,A=1000,x=structure(.Data = c(
.4801,.1142,.1003,.0376,.0275,.0363,.0568,.0636,.0429,.0407,
.5500,.0500,.0500,.0700,.1000,.0000,.0200,.1500,.0000,.0100,
.4200,.2000,.0500,.0700,.0000,.0800,.0200,.1400,.0100,.0100,
.5700,.2000,.0900,.0100,.0200,.0800,.0200,.0000,.0000,.0100,
.5700,.0500,.0700,.0700,.0000,.0000,.1500,.0800,.0000,.0100,
.4400,.2000,.0500,.0700,.0000,.0000,.0200,.0000,.1200,.1000,
.5700,.0500,.0964,.0100,.1000,.0000,.0336,.0000,.1300,.0100,
.5363,.0500,.0837,.0100,.0000,.0800,.1500,.0000,.0800,.0100,
.4200,.1962,.0538,.0100,.0000,.0800,.1400,.0000,.0000,.1000,
.5700,.0851,.0941,.0100,.0000,.0000,.0200,.1200,.0000,.1000,
.4200,.1549,.0751,.0100,.1000,.0000,.0200,.1400,.0000,.0800,
.4200,.1764,.0736,.0700,.1000,.0000,.1500,.0000,.0000,.0100,
.5700,.2000,.1862,.0100,.0000,.0000,.0200,.0038,.0000,.0100,
.4200,.2000,.1862,.0100,.0000,.0000,.0200,.0238,.1300,.0100,
.5589,.0500,.1211,.0700,.0000,.0800,.0200,.0000,.0000,.1000,
.4327,.0500,.1873,.0100,.0000,.0800,.0858,.1442,.0000,.0100,
.4545,.0500,.1455,.0100,.1000,.0000,.1400,.0000,.0000,.1000,
.4214,.0500,.1186,.0700,.0200,.0800,.0200,.0000,.1300,.0900,
.4801,.1142,.1003,.0376,.0275,.0363,.0568,.0636,.0429,.0407,
.4801,.1142,.1003,.0376,.0275,.0363,.0568,.0636,.0429,.0407,
.5700,.2000,.0900,.0100,.0200,.0800,.0200,.0000,.0000,.0100,
.5363,.0500,.0837,.0100,.0000,.0800,.1500,.0000,.0800,.0100,
.5153,.0956,.1052,.0375,.0289,.0084,.1179,.0456,.0063,.0393
), .Dim = c(23,10)),
y=c(5.78,13.29,2.39,8.70,13.24,2.01,72.88,29.26,4.06,
83.83,14.50,0.42,3.31,3.42,2.55,17.81,2.23,1.87,5.76,
5.71,9.36,38.11,5.69)
)
Inits
list(tau=4)
```

TABLE 7. WinBUGS Results for Fitting the First-Degree Mixture Model to the CVS-I $\log_e$(viscosity) Data

			Posterior quantile				
Term	Mean	SD	0.025	0.05	0.5	0.95	0.975
SiO_2	8.79	0.44	7.92	8.07	8.78	9.471	9.65
B_2O_3	−6.57	0.76	−8.13	−7.83	−6.54	−5.41	−5.21
Na_2O	−11.20	1.24	−13.59	−13.12	−11.24	−9.16	−8.65
Li_2O	−33.21	2.00	−37.08	−36.43	−33.32	−29.79	−29.12
CaO	−4.49	1.65	−7.62	−7.19	−4.57	−1.80	−1.23
MgO	−0.93	1.64	−4.10	−3.39	−1.07	1.91	2.59
Fe_2O_3	−0.48	1.04	−2.49	−2.15	−0.43	1.19	1.60
Al_2O_3	11.02	1.02	8.92	9.33	11.08	12.62	13.07
ZrO_2	8.43	1.17	6.03	6.46	8.46	10.37	10.73
Others	−0.36	1.37	−3.14	−2.66	−0.34	1.73	2.26
σ	0.1483	0.0938	0.0028	0.0049	0.1473	0.3055	0.3447

one such model in which there is a constant coefficient of variation, δ.

One referee pointed out a number of other situations in which mixture errors arise that suggest the need for further model development. Besides errors in measuring masses or volumes of components, there can be blending or processing errors (such as errors in calculating or weighing amounts of precursor chemicals in addition to impurities) if a chemical reaction is involved. There may also be errors in analyzing the composition of what was obtained. While modeling these more complicated situations is beyond the scope of this article, a Dirichlet distribution (Kotz and Johnson (1982)) for the mixture proportions might be considered.

Once an appropriate mixture error model is developed, its parameters need to estimated. For the absolute mixture error model considered in this article, in which the component amount errors are independent, inference on the variance σ^2_{mix} can be obtained by repeatedly weighing out amounts and comparing them with the intended amounts. The resulting uncertainty of the variance σ^2_{mix} from such studies can also be accounted for in the Bayesian

TABLE 8. WinBUGS Results for Fitting the First-Degree Mixture Model to the CVS-I $\log_e$(viscosity) Data That Ignores Mixture Errors

			Posterior quantile				
Term	Mean	SD	0.025	0.05	0.5	0.95	0.975
SiO_2	8.81	0.56	7.71	7.88	8.81	9.75	9.95
B_2O_3	−6.68	0.93	−8.57	−8.21	−6.68	−5.18	−4.83
Na_2O	−11.21	1.54	−14.36	−13.76	−11.20	−8.72	−8.08
Li_2O	−33.10	2.46	−37.88	−37.07	−33.12	−29.05	−28.14
CaO	−4.28	1.75	−7.73	−7.12	−4.30	−1.39	−0.80
MgO	−0.82	1.83	−4.49	−3.88	−0.81	2.21	2.78
Fe_2O_3	−0.53	1.16	−2.80	−2.42	−0.55	1.37	1.87
Al_2O_3	10.94	1.22	8.57	8.97	10.93	12.97	13.41
ZrO_2	8.45	1.33	5.85	6.32	8.45	10.65	11.13
Others	−0.49	1.56	−3.56	−3.04	−0.49	2.08	2.60
σ	0.2798	0.0602	0.1893	0.1998	0.2707	0.392	0.4233

TABLE 9. CVS-I Predicted Viscosities When Mixture Errors Are Either Considered or Ignored

	Mixture errors included				Mixture errors ignored			
Glass	Mean	SD	0.05	0.95	Mean	SD	0.05	0.95
CVS1-1	6.37	1.51	4.56	9.13	7.39	2.26	4.43	11.33
CVS1-2	14.90	3.92	10.39	22.12	17.82	6.43	9.75	29.43
CVS1-3	2.60	0.66	1.80	3.81	2.95	1.09	1.57	4.86
CVS1-4	8.99	2.16	6.08	12.71	9.34	3.33	5.11	15.19
CVS1-5	12.60	2.98	8.08	17.29	11.42	4.25	5.97	19.15
CVS1-6	2.00	0.50	1.31	2.82	1.98	0.76	1.04	3.32
CVS1-7	65.33	15.54	39.76	88.23	53.52	20.46	27.92	90.14
CVS1-8	33.22	9.16	23.40	49.24	40.30	13.98	22.07	66.01
CVS1-9	3.98	0.93	2.59	5.52	3.77	1.39	2.00	6.24
CVS1-10	82.60	19.61	53.94	115.10	80.24	30.19	42.27	132.90
CVS1-11	14.17	3.39	9.20	19.67	13.54	5.14	7.15	22.37
CVS1-12	0.39	0.09	0.25	0.53	0.35	0.13	0.18	0.59
CVS1-13	3.55	1.00	2.42	5.19	3.92	1.58	2.05	6.54
CVS1-14	3.61	0.91	2.43	5.19	3.91	1.48	2.03	6.56
CVS1-15	2.49	0.61	1.59	3.51	2.35	0.91	1.20	3.95
CVS1-16	16.02	3.76	9.78	21.62	13.03	4.93	6.79	22.07
CVS1-17	2.64	0.77	1.80	4.06	3.37	1.28	1.78	5.68
CVS1-18	1.92	0.48	1.27	2.75	1.99	0.76	1.03	3.35
CVS1-19	6.35	1.56	4.54	9.08	7.40	2.32	4.42	11.40
CVS1-20	6.32	1.52	4.53	9.12	7.39	2.30	4.41	11.44
CVS1-21	9.36	2.30	6.25	12.99	9.33	3.39	5.06	15.29
CVS1-22	38.94	9.29	25.93	55.20	40.18	14.01	22.06	65.23
CVS1-23	6.02	1.42	4.16	8.48	6.49	2.04	3.79	10.11

analysis of mixture experiments. Instead of σ^2_{mix} being a constant, its uncertainty may be reflected by an appropriate distribution such as an inverse gamma distribution. For other mixture error models suggested above, appropriate studies and inference may require additional research.

Conclusions

We have shown how a Bayesian approach can account for mixture errors in analyzing mixture experiments. The benefits of using such an approach are better estimates of the response model error variance, which leads to better inference, including better predictions and shorter prediction intervals. This work suggests a number of research problems, which include modeling mixture errors and assessing them through appropriately designed studies. With different mixture error models, it will be interesting to see how they impact the analysis of mixture experiments.

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