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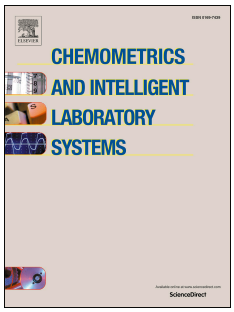
Accepted Manuscript



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PII: S0169-7439(18)30237-5

DOI: 10.1016/j.chemolab.2018.09.004

Reference: CHEMOM 3680

To appear in: *Chemometrics and Intelligent Laboratory Systems*

Received Date: 18 April 2018

Revised Date: 10 September 2018

Accepted Date: 13 September 2018

Please cite this article as: R.N.B. da Silva, F. Pennecchi, D.B. Hibbert, I. Kuselman, Tutorial and spreadsheets for Bayesian evaluation of risks of false decisions on conformity of a multicomponent material or object due to measurement uncertainty, *Chemometrics and Intelligent Laboratory Systems* (2018), doi: https://doi.org/10.1016/j.chemolab.2018.09.004.

Tutorial and spreadsheets for Bayesian evaluation of risks of false decisions on conformity of a multicomponent material or object due to measurement uncertainty

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Abstract A tutorial and a user-friendly program for evaluating risks of false decisions in conformity assessment of a multicomponent material or object due to measurement uncertainty, based on a Bayesian approach, are presented. The developed program consists of two separate MS-Excel spreadsheets. It allows calculation of the consumer's and producer's risks concerning each component of the material whose concentration was tested ('particular risks') as well as concerning the material as a whole ('total risks'). According to the Bayesian framework, probability density functions of the actual/'true' component concentrations (prior pdfs) and likelihood functions (likelihoods) of the corresponding test results are used to model the knowledge about the material or object. Both cases of independent and correlated variables (the actual concentrations and the test results) are treated in the present work. Spreadsheets provide an estimate of the joint posterior pdf for the actual component concentrations as the normalized product of the multivariate prior pdf and the likelihood, starting from normal or log-normal prior pdfs and normal likelihoods, using Markov Chain Monte Carlo (MCMC) simulations by the Metropolis-Hastings algorithm. The principles of Bayesian inference and MCMC are described for users with basic knowledge in statistics, necessary for correct formulation of a task and interpretation of the calculation results. The spreadsheet program was validated by comparison of the obtained results with analytical results calculated in the R programming environment. The developed program allows estimation of risks greater than 0.003 % with standard deviations of such estimates spreading from 0.001 % to 1.5 %, depending on the risk value. Such estimation characteristics are satisfactory, taking into account known variability in measurement uncertainty associated with the test results of multicomponent materials.

Keywords Conformity assessment · Risk of false decision · Measurement uncertainty · Multicomponent material · Markov Chain Monte Carlo simulations · Spreadsheet

1. Introduction

Properties of multicomponent materials, such as medications, alloys, food and clinical samples, and objects (e.g. ambient air), depend on actual/'true' concentration c_i of the i-th component, $i = 1, 2, \ldots, n$, which is measured during conformity assessment. Note, the term concentration is used here as a general concept, since concentration is the most frequent type of measured quantity in chemistry. However, the discussion in this paper is also applicable to other quantities, such as pH, Brix, total organic carbon, etc.

The material or object is considered 'conforming' when c_i values are in the specification, regulation or legal tolerance limits/intervals $[T_{Li}, T_{Ui}]$, where T_{Li} and T_{Ui} are lower and upper limits of the interval, respectively. Comparing chemical analytical measurement/test result c_{im} of the concentration of i-th component with the upper limit T_{Ui}, for example, one can decide whether the material or object conforms or not. Since any measurement result c_{im} has an associated measurement uncertainty [1, 2], two kinds of risk of a false decision on conformity may arise. The probability of the false decision that the component concentration does not exceed the upper limit, based on the measurement result $c_{im} \leq T_{Ui}$, when the material actually does not conform, i.e. the actual concentration exceeds the upper limit ($c_i > T_{Ui}$), is 'consumer's risk'. On the other hand, the probability of falsely rejecting the decision on conformity (i.e. $c_{im} > T_{Ui}$ when in fact $c_i \leq T_{Ui}$) is the 'producer's risk'.

For a specified material batch, lot, or an environmental compartment, e.g. ambient air in a certain location at a certain time, such risks are referred to as the 'specific consumer's risk, $R^*_{ci(c)}$, and the 'specific producer's risk', $R^*_{ci(p)}$, respectively, for the i-th component. The risks of incorrect conformity assessment of a batch randomly drawn from a statistical population of such batches are the 'global consumer's risk', $R_{ci(c)}$, and the 'global producer's risk', $R_{ci(p)}$, respectively, as they characterize the material quality globally. Evaluation of the both specific and global risks for a particular (single) component i is described in the JCGM guidelines [3] based on a Bayesian framework for assessing conformity.

Besides the specification limits for actual concentration values c_i, acceptance limits for measurement results c_{im} can be applied taking into account the measurement uncertainty. In such a case, the decision rules are formulated based on comparison of the measurement/test results with the acceptance limits, thereby reducing the consumer's or producer's risk [3, 4].

When concentrations of two or more components are controlled, component-by-component evaluation of the risks is not complete in general, as it does not give an answer to the question of the probability of a false decision on conformity of the overall material or

object. If conformity assessment for each *i*-th component concentration of a specified batch of a material is successful (i.e. the particular specific risks, R^*_{ci}, are small enough), the total probability of a false decision concerning conformity of the material as a whole (i.e. the *total* specific risk R^*_{total}) might still be significant. The evaluation of total risks is the task of the IUPAC project [5]. In the framework of this project, it was shown, based on the law of total probability, that the total risk can be evaluated as a combination of the particular risks, whenever the variables (c_i and c_{im}) are independent. A model of the total consumer's risk was formulated and applied for customs control of completely denatured alcohols, where conformity assessment was performed by comparison of chemical analytical test results with the lower regulatory limits for concentrations of three denaturants. The model was based on assumptions of the normal prior probability density functions (pdfs) of actual denaturant concentrations and the normal likelihood functions (likelihoods) of the test results [6].

A similar model for the total producer's risk was developed and used for a case of total suspended particulate matter (TSPM) concentration in ambient air near three independent stone quarries located in Israel, as the sources of air pollution. The conformity decisions were based here on comparison of TSPM test results with the national upper regulation limit. In this case, the actual TSPM concentrations were described by prior lognormal pdfs, whereas the likelihoods of the test results were assumed to be normal. Total probabilities of underestimation of TSPM concentration (total consumer's risk of the inhabitants) and overestimation (total risk of the stone producers) were evaluated as a combination of the particular risks of air conformity assessment concerning TSPM concentrations for each quarry [7].

In the paper [8], the probability of a false decision on conformity of a medication due to measurement uncertainty was discussed when test results of four active components of the medication are correlated. Specification limits of the components' contents of such a medication generate a multivariate specification interval/domain [9]. Actual values of components' content and corresponding test results were modelled by multivariate normal prior pdf and likelihood function. It was shown that the influence of the correlation on the risk values is not easily predictable.

The total risks of false decisions on conformity of a platinum-rhodium alloy batch due to measurement uncertainty were also quantified for four components, when a strong correlation of test results was observed [10]. As in the previous work [8], actual values of components' content and corresponding test results were modelled by multivariate normal prior pdf and likelihood function. It was found that simplification of the testing by reducing the number of

components under control (taking one component of two for which the test results are strongly correlated) leads to a significant underestimation of the probability of a false decision on conformity of the alloy.

Calculation of the specific risks in these studies [6-8, 10] was based on the analytical expressions (or corresponding numerical approximations) of the posterior pdf for the actual component concentrations as the normalized product of the multivariate prior pdf and the likelihood, performed within the R programming environment [11]. In parallel with the R codes, a user-friendly MS-Excel program was developed based on the same Bayesian approach, but implemented through the Markov Chain Monte Carlo (MCMC) method.

The present paper is a tutorial for quantification of specific risks in conformity assessment of multicomponent materials due to measurement uncertainty, making more accessible the developed concepts and necessary computational tools. Principles of the Bayesian approach and MCMC method are explained for correct formulation of the risk estimation task and interpretation of the results. The validated spreadsheets for calculation of specific risks are available as supplementary electronic material. Similar spreadsheeds for evaluation of global risks will be worked out in the continuation of the IUPAC project [5].

2. Theory

Bayesian inference provides a probability distribution of a component concentration as a posterior pdf, starting from prior knowledge about the component in the material or object before the measurement (the prior pdf or simply ‘prior’), updated by new information coming from measurement results modelled by the likelihood function (‘likelihood’) [12].

The prior is obtained from available information on component concentrations in similar batches of the material or objects. The batch-to-batch distribution of measurement results, accumulated during testing a large enough number of batches, lots or environmental compartments, can be used as prior, when the measurement uncertainty is negligible in comparison to the batch-to-batch variation. The assumption is that the actual concentration values are approximated by the measurement/test results adequately ($c_i \approx c_{\mathrm{im}}$). If there is no detailed prior knowledge about the component concentration in the tested material or object, the prior pdf is vague. In such cases, a uniform pdf may be used, limited by the lowest and the highest possible values for the component concentration.

The likelihood is a function describing the plausibility of the actual values of a component concentration at a given measurement result. In practice, a distribution $p(c_{im}|c_i)$ of

measurement results at a given actual component concentration value c_i, i.e. related to one and the same sample, is usually available from the analytical method validation data. This distribution of the measurement results, regarded as a function of c_i, is nothing else than the likelihood function itself.

The posterior distribution of c_i (the posterior pdf) is the normalized product of the prior and the likelihood.

Two spreadsheets have been developed for calculating the posterior pdf for a particular component, as well as the joint posterior pdf for up to four components of a material or object. The spreadsheets allow evaluation of the specific risks of false decisions about conformity of a component concentration separately (i.e. the particular specific risks R_{ci}^{*}), and considering the material or object as a whole (i.e. the total specific risk R_{total}^{*}). One spreadsheet is designed for uncorrelated test results (UnCorrel4Risk.xlsm) and the other for correlated test results (Correl4Risk.xlsm). Both the spreadsheets process multivariate normal prior pdfs and likelihoods, but the file 'UnCorrel4Risk.xlsm'can also process prior log-normal pdfs. The spreadsheets' files and videos explaining the use of these files are available as Electronic Supplementary Material.

The concentrations measured in the studied objects can be correlated due to intrinsic correlations of the actual concentrations c_i of the material or object, or due to the correlation of the measurement results c_{im}. Intrinsic correlations are derived from stoichiometric or mass balance limitations, or are due to technological reasons. When composition of a material or object is expressed as sum of mass fractions or mole fractions equal to 100 %, correlation among them may be spurious [13, 14]. The 'metrological' correlation occurs because of interaction of the components at different steps of the measurement process (chemical analysis) or because of interferences of the analytical signals, e.g. in a spectral analysis [8]. In this tutorial, the origin of the correlation between results is not distinguished, hence the same correlation matrix being used for both c_i and c_{im}.

2.1. Bayesian estimate of a concentration

For an easier understanding of Bayes theorem, its application is firstly illustrated using a specific example involving Boolean variables and then described for continuous variables such as component concentrations in a material or object.

2.1.1. Bayes theorem for Boolean variables

The probability $P(\mathrm{A}|\mathrm{E})$ of an event A (e.g. the pregnancy of a 28-year-old woman) when some discrete evidence E is observed (e.g. a colour change of a test kit exposed to the urine of the woman), i.e. the probability of A given E, is:

$$P(\mathrm{A}|\mathrm{E}) = \frac{P(\mathrm{A})P(\mathrm{E}|\mathrm{A})}{P(\mathrm{E})}, \tag{1}$$

where $P(\mathrm{A})$ is the prior probability of the event A, $P(\mathrm{E}|\mathrm{A})$ the probability of observing E given the event A, and $P(\mathrm{E})$ is the probability of the evidence E being observed [12]. In other words, in this example $P(\mathrm{A})$ is the probability of a 28-year-old woman being actually pregnant, $P(\mathrm{E}|\mathrm{A})$ is the probability of the test kit producing a colour change when testing the urine of a pregnant woman, and $P(\mathrm{E})$ is the probability of the test producing a colour change regardless of the pregnancy status of the woman. Probability $P(\mathrm{E})$ by the law of total probability is $P(\mathrm{E}) = P(\mathrm{A})P(\mathrm{E}|\mathrm{A}) + P(\neg\mathrm{A})P(\mathrm{E}|\neg\mathrm{A})$, where $P(\neg\mathrm{A}) = 1 - P(\mathrm{A})$ is the probability of the woman being not pregnant, and $P(\mathrm{E}|\neg\mathrm{A})$ is the probability of observing a colour change of the test kit when the woman is not pregnant – false positive probability. Equation (1) shows that the prior probability $P(\mathrm{A})$ of the woman pregnancy is modified after observation E of the colour change of the test kit into the posterior probability $P(\mathrm{A}|\mathrm{E})$.

If a test result of a 44-year-old woman is positive for pregnancy, the corresponding probability of actual pregnancy $P(\mathrm{A}|\mathrm{E})$ will be smaller than that of a 28-year-old woman showing the same positive test result. In fact, considering $P(\mathrm{E}|\mathrm{A})$ fixed as a property of the test kit, according to equation (1), $P(\mathrm{A}|\mathrm{E})$ decreases if $P(\mathrm{A})$ decreases, as happens for women older than 28-years-old.

Moreover, in order to be more confident about the probability of actual pregnancy for a 44-year-old woman showing a positive test E, a second test kit could be used for the same woman. Let us suppose the results of the two test kits are conditionally independent, that is, $P(\mathrm{E},\mathrm{F}|\mathrm{A}) = P(\mathrm{E}|\mathrm{A})\,P(\mathrm{F}|\mathrm{A})$. Hence, the probability $P(\mathrm{A}|\mathrm{E},\mathrm{F})$ of the women being pregnant, where F is the evidence of pregnancy by the second test kit, is:

$$P(\mathrm{A}|\mathrm{E},\mathrm{F}) = \frac{P(\mathrm{A})P(\mathrm{E}|\mathrm{A})P(\mathrm{F}|\mathrm{A})}{P(\mathrm{A})P(\mathrm{E}|\mathrm{A})P(\mathrm{F}|\mathrm{A}) + P(\neg\mathrm{A})P(\mathrm{E}|\neg\mathrm{A})P(\mathrm{F}|\neg\mathrm{A})}, \tag{2}$$

where $P(\mathrm{F}|\mathrm{A})$ and $P(\mathrm{F}|\neg\mathrm{A})$ are the probabilities of the second test kit indicating pregnancy when the woman is actually pregnant or not, respectively.

After the second evidence, the posterior probability increases from $P(\mathrm{A}|\mathrm{E})$ to $P(\mathrm{A}|\mathrm{E},\mathrm{F})$ suggesting that the woman is more likely pregnant when she has a positive evidence from both the tests. $P(\mathrm{A}|\mathrm{E},\mathrm{F})$ is greater than $P(\mathrm{A}|\mathrm{E})$, in fact, because the true positive rate of the second test $P(\mathrm{F}|\mathrm{A})$ is greater than the false positive rate $P(\mathrm{F}|\neg\mathrm{A})$. For example, assuming probability of a 44-year-old woman being pregnant $P(\mathrm{A})$ = 0.019, probability of test kits correctly detecting a pregnancy – true positive $P(\mathrm{E}|\mathrm{A}) = P(\mathrm{F}|\mathrm{A})$ = 0.985, and probability of test kits incorrectly declaring a pregnancy – false positive $P(\mathrm{E}|\neg\mathrm{A}) = P(\mathrm{F}|\neg\mathrm{A})$ = 0.008, hence $P(\mathrm{A}|\mathrm{E}) = 0.019 \cdot 0.985/(0.019 \cdot 0.985 + (1 - 0.019) \cdot 0.008) = 0.704$ and $P(\mathrm{A}|\mathrm{E},\mathrm{F}) = 0.985^2 \cdot 0.019/(0.019 \cdot 0.985^2 + (1 - 0.019) \cdot 0.008^2) = 0.997$. The results from the second test kit updates the posterior information from the first kit. The posterior probability is the same when the second kit is used first, as can be observed from formula (2): $P(\mathrm{A}|\mathrm{E},\mathrm{F}) = P(\mathrm{A}|\mathrm{F},\mathrm{E})$.

The Bayesian approach has the advantage of accurately reproducing the decision process based on cumulative evidence of an event, in particular, when independent evidences of the event are collected. Naturally, this approach depends on the adequacy of the prior information.

The example above describes the application of the Bayes theorem to Boolean variables (e.g. colour change: ‘yes’ or ’no’). However, this theorem is also applicable to continuous variables such as concentrations.

2.1.2. Bayes theorem for continuous variables

The description of the occurrence of concentration c_i is modelled by a pdf, describing how the probability density $p(c_i)$ varies with the concentration value. The probability of c_i being in the range $[a_1, a_2]$ is:

$$P(a_1 \leq c_i \leq a_2) = \int_{a_1}^{a_2} p(c_i)\, dc_i \,. \tag{3}$$

Regardless of the type of the distribution of c_i values, the lowest and highest limits of a 95 % coverage interval of the values, for example, are percentiles b_1 and b_2 such that $P(c_i \leq b_1) =$ 2.5 % and $P(c_i \leq b_2) = 97.5$ %, that is:

$$P(b_1 \leq c_i \leq b_2) = \int_{b_1}^{b_2} p(c_i)\, dc_i = 95\ \% \,. \tag{4}$$

Application of Bayes theorem provides estimate of an actual concentration c_i given a measurement result c_{im}. Since both the concentration value and the measurement result are continuous variables, the (mass) probabilities discussed in Section 2.1.1 are substituted here for corresponding (continuous) pdfs [12]:

$$p(c_i|c_{im}) = \frac{p(c_{im}|c_i)p(c_i)}{p(c_{im})}, \tag{5}$$

where denominator $p(c_{im}) = \int p(c_{im}|c_i)p(c_i)dc_i$ is the normalizing constant factor.

The posterior probability $P(q_1 \le c_i \le q_2|r_1 \le c_{im} \le r_2)$ of c_i being between q_1 and q_2 given c_{im} varying between r_1 and r_2 is proportional to the following double integral:

$$P(q_1 \le c_i \le q_2|r_1 \le c_{im} \le r_2) \propto \int_{q_1}^{q_2}\int_{r_1}^{r_2} p(c_{im}|c_i)\, p(c_i)dc_{im}dc_i, \tag{6}$$

where symbol $\propto$ indicates proportionality. The probability of the concentration c_i being between q_1 and q_2 is:

$$P(q_1 \le c_i \le q_2|c_{im}) \propto \int_{q_1}^{q_2} p(c_{im}|c_i)\, p(c_i)dc_i\,. \tag{7}$$

The Markov Chain Monte Carlo (MCMC) method is helpful for numerical estimation of $p(c_i|c_{im})$ by formula (5), since it allows us to skip the normalizing constant factor $p(c_{im})$ [12, 15].

2.2. Markov Chain Monte Carlo Method

The MCMC method is initiated by setting a starting point, α, close to the expected mode of the distribution of the posterior concentration, which is usually positioned between the modes of the prior pdf and likelihood function. In many cases, α can be chosen as the mode of the prior or the likelihood. As a first step, the prior and the likelihood at α, i.e. $p(c_i = \alpha)$ and $p(c_{im}|c_i = \alpha)$ respectively shown in Fig. 1, are calculated according to the relevant analytical expressions.

Fig. 1

For instance, if $p(c_i)$ is a lognormal pdf, as in Fig. 1a, probability density $p(\alpha)$ at the starting point is calculated by the following formula:

$$p(\alpha) = \frac{1}{\alpha s_{gi}\sqrt{2\pi}} \exp\left(-\frac{\left(\ln(\alpha) - \mu_{gi}\right)^2}{2s_{gi}^2}\right), \quad (8)$$

where μ_{gi} and s_{gi} are the geometric mean and geometric standard deviation of the prior distribution of c_i values, respectively, hence satisfying μ_{gi}= exp($\mu_{\ln(c_i)}$) and s_{gi}= exp($s_{\ln(c_i)}$), where $\mu_{\ln(c_i)}$ and $s_{\ln(c_i)}$ are the mean and standard deviation of the (normal) distribution of ln(c_i) values. The pdf (8) is calculated in MS-Excel using function LOGNORM.DIST(α, μ_{gi}, s_{gi}, FALSE).

If the prior is a normal pdf, corresponding probability density values $p(\alpha)$ are generated by using MS-Excel function NORM.DIST(α, μ_i, s_i, FALSE).

When $p(c_{im}|c_i)$ is a normal pdf (shown in Fig 1b as the likelihood function of c_i at a given c_{im}), the probability density at the starting point is:

$$p(c_{im}|c_i = \alpha) = \frac{1}{u_i\sqrt{2\pi}} \exp\left(-\frac{1}{2}\left(\frac{c_{im} - \alpha}{u_i}\right)^2\right), \quad (9)$$

where u_i is the standard uncertainty associated with c_{im}. This probability is calculated in MS-Excel using function NORM.DIST(α, c_{im}, u_i, FALSE).

The posterior pdf is given by multiplying $p(\alpha)$ by $p(c_{im}|\alpha)$.

Then, a new value of c_i, denoted as β, is generated by randomly drawing a value from a normal transition distribution [12] with mean α and standard deviation t, where t is designated the Markov Chain increment. The MS-Excel NORM.INV(RAND(), α, t) is used to produce β. The increment is defined from a normal transition distribution, regardless of the prior distribution and the likelihood function.

The posterior pdf at $c_i = \beta$ is given by $p(\beta)p(c_{im}|\beta)$. If the prior and the likelihood are log-normal and normal, respectively, $p(\beta)$ and $p(c_{im}|\beta)$ are calculated according to Eqs (8) and (9), respectively, after substituting α for β.

To decide if β is to be retained for the next iteration, the ratio $r(\beta, \alpha)$ is calculated according to:

$$r(\beta, \alpha) = \frac{p(\beta)p(c_{im}|\beta)}{p(\alpha)p(c_{im}|\alpha)}. \quad (10)$$

If $r(\beta, \alpha)$ is greater than one or than a value randomly generated from an uniform distribution on (0, 1) with MS-Excel function RAND(), β is retained for the following iteration, otherwise α is considered for a new iteration. The new iteration is generated using NORM.INV(RAND(), β, t) or NORM.INV(RAND(), α, t), respectively. At each iteration, a ratio equivalent to that in equation (10) is estimated and a new value from uniform distribution on (0,1) is drawn to decide which value to retain for the next iteration. This sampling method of the posterior distribution is known as the 'Metropolis–Hastings algorithm' [12, 15].

The process is repeated many times with the new or the previous value of the iteration being retained. As the iteration progresses, the simulated value approaches the mode of the posterior pdf and the simulation starts sampling values above and below the mode proportionally to their density. The *a-posteriori* retained concentration values estimate the probability density $p(c_i|c_{im})$.

A graphical representation of the retained c_i during the iterations progress allows to assess if the mode of $p(c_i|c_{im})$ has been reached and if the posterior pdf was sampled correctly. Fig. 2 illustrates the impact of the increment size *t* on sampling the posterior pdf.

Fig. 2

As shown in Fig. 2a, a small value of *t* may not allow the process to reach the mode of $p(c_i|c_{im})$ even if α is close to it. A large value of *t*, as in Fig. 2b, makes it likely that an iteration will produce the new c_i value with corresponding $p(c_i|c_{im})$ smaller than that in the previous iteration, hence causing rejection of the new value. This process reduces the number of iterations used to describe $p(c_i|c_{im})$ thus wasting computational time. Fig. 2c, when an adequate *t* is used, c_i values are presented as a noisy line.

If the starting point of the Markov Chain process is far away from the mode of the posterior distribution, it is convenient to reject the first iterations since they are not representative. The so-called "burn-in period" set for the Markov Chain defines the number of initial rejected iterations for the characterisation of the posterior distribution [12, 15].

It is also advisable to take only each third or fifth iteration to avoid creating an artificial correlation between simulated values. The "thinning interval" set for the Markov Chain defines this additional filtration of data [12, 15].

The posterior distribution of simulated c_i values can be characterised by percentiles that define the lower and higher limits of specific coverage intervals or, if the posterior distribution is normal, by the mean and the standard deviation of the generated c_i values.

The MCMC method can be applied also for simulation of concentrations of two and more independent components of a material or object simultaneously, for example concentrations c_1

and c_2 of a pair of a material components. A point here is a vector $\boldsymbol{c_{12}}$ consisting of c_1 and c_2 (posterior concentrations of the first and the second components). Sizes of independent increments t_1 and t_2 of c_1 and c_2 values, respectively, form vector $\boldsymbol{t_{12}}$. The newly generated vector ($\boldsymbol{c_{12}} + \boldsymbol{t_{12}}$) is only retained if the ratio between the joint pdf of ($c_1 + t_1$) and c_1 and the ratio between the joint pdf of ($c_2 + t_2$) and c_2 are greater than 1 or than two randomly generated values from an uniform distribution on (0, 1).

Selection of the starting point and the vector of the increment sizes should allow a representative sampling of the posterior bivariate distribution. Fig. 3 demonstrates some cases of posterior pdf sampling at different vectors $\boldsymbol{t}$ of the increments' sizes.

Fig. 3

2.3. Posterior distribution of correlated variables

If concentrations of different components of a material or object are correlated (both the actual values and the corresponding test results), it is necessary to take the correlation into account when estimating the parameters of the posterior multivariate (joint) pdf for the tested concentrations of the components.

In general, a multivariate normal pdf of n component concentrations c_i, i = 1, 2, …, n, is characterised by a vector $\boldsymbol{\mu}$ of means of the component concentrations (μ_1, μ_2, …, μ_n) and a covariance matrix $\boldsymbol{\Sigma}$ expressing the variances of the concentrations and the covariance between them [8, 16].

If the prior is a multivariate normal pdf, the prior probability density $p(\boldsymbol{c})$ of a vector $\boldsymbol{c}$ of the concentrations (c_1, c_2, …, c_n) is [20]:

$$p(\boldsymbol{c}) = \frac{\exp\left(-\frac{1}{2}(\boldsymbol{c}-\boldsymbol{\mu})^{\mathrm{T}}\boldsymbol{\Sigma}^{-1}(\boldsymbol{c}-\boldsymbol{\mu})\right)}{\sqrt{(2\pi)^n|\boldsymbol{\Sigma}|}}, \tag{11}$$

where $(\boldsymbol{c}-\boldsymbol{\mu})^{\mathrm{T}}$ is the transpose vector of the $(\boldsymbol{c}-\boldsymbol{\mu})$ and $|\boldsymbol{\Sigma}|$ is the determinant of the covariance matrix. A multivariate normal likelihood $p(\boldsymbol{c_m}|\boldsymbol{c})$ is similar to (11), with $p(\boldsymbol{c_m}|\boldsymbol{c})$, $\boldsymbol{c_m}$, $\boldsymbol{c}$ and $\boldsymbol{\Sigma_m}$ substituting for $p(\boldsymbol{c})$, $\boldsymbol{c}$, $\boldsymbol{\mu}$ and $\boldsymbol{\Sigma}$, respectively, where $\boldsymbol{c_m}$ is the vector of the measured components concentrations, and $\boldsymbol{\Sigma_m}$ is the covariance matrix, built using measurement standard uncertainties associated with c_{im} and estimated correlations between them.

Formula (11) can be implemented in MS-Excel using functions for operations with matrices (e.g. MMULT(array1, array2) for multiplication of two matrices), or by performing matrix calculations reproducing respective algebraic relations.

2.4. Calculation of risks

When one component i of an object is studied, the probability that the object does not conform, P_{nc}, can be estimated as the relative frequency of simulated posterior concentrations, c_i, falling outside the tolerance limits [$T_{\mathrm{L}i}$, $T_{\mathrm{U}i}$]. When c_{im} is within the tolerance limits, P_{nc} is the specific particular consumer's risk, $R^*_{ci(\mathrm{c})}$, while if c_{im} is outside the limits, (1– P_{nc}) is the specific particular producer's risk, $R^*_{ci(\mathrm{p})}$.

When two or more components of the object are studied, the relative frequency of the simulated posterior concentration vectors, where at least one c_i is outside its limits, is calculated. This relative frequency is an estimate of the probability that the object does not conform, P_{nc}. When all c_{im} are within their specification limits, P_{nc} is an estimate of the specific total consumer's risk, $R^*_{\mathrm{total(c)}}$, while when at least one c_{im} is outside the limits, (1– P_{nc}) estimates the specific total producer's risk $R^*_{\mathrm{total(c)}}$.

3. Spreadsheets

Two spreadsheets have been developed to estimate the specific risks (both particular and total) of false decisions on conformity of a material or object to the tolerance limits $T_{\mathrm{L}i}$ and $T_{\mathrm{U}i}$, when up to four component concentrations are measured/tested.

The first spreadsheet (UnCorrel4Risk.xlsm) is applicable to materials or objects when correlation of test results for different components is negligible, each prior pdf is normal or lognormal and each likelihood is normal.

The second spreadsheet (Correl4Risk.xlsm) is applicable when correlation of test results is statistically significant, while both the joint prior pdf and the joint likelihood are normal.

These spreadsheets are used by selecting the number n of studied components(variables) in cell E7, entering the name of the components, the distributional family, the parameters of the prior pdf and the likelihood (mean and standard deviation for a normal pdf, geometric mean and standard deviation for a lognormal pdf), the tolerance limits $T_{\mathrm{L}i}$ and $T_{\mathrm{U}i}$, and the configuration parameters of the Markov Chain. For the spreadsheet processing correlated test results (Correl4Risk.xlsm), the types of the distributions are not to be selected since it is applicable to

normal distributions only. Pearson correlation coefficients for all pairs of the components should be entered in this spreadsheet for specification of the covariance matrix.

The parameters of the Markov chain are the starting point of the chain, typically the available measurement/test result c_{im}, the increments, the burn-in period and the thinning interval. The optimisation of the increment is performed by checking how different values of increments affect the Markov chain as discussed in section 2.2. Half of the standard measurement uncertainty u_i of c_{im} is usually a good initial value for increment optimisation.

The burn-in period is between 100 and 1000, if the starting point of the Markov chain is not far from the mode of the posterior pdf. A thinning interval of 3 or 5 is enough to avoid correlation of generated results.

Since the initial stage of the MS-Excel files perform just 50 to 100 simulations, before optimising the Markov chain, for estimating $p(c_i|c_{im})$ and the specific risks it is necessary to increase the number of simulations. This is possible by pressing “Crtl+q” for 15000 and “Ctrl+i” for 150000 simulations, or by using corresponding buttons of the spreadsheet. The recalculate button or “F9” can be used to obtain a new set of simulations. “Ctrl+h” can reduce simulations back to 50 or 100 to allow saving input data in a small file.

A file with 150000 lines needs only a few seconds to perform a new set of 150000 iterations. However, the increase of lines to 150000 takes about 3 min to compute.

The mean of specific risks estimated from 30 or 40 sets of simulations can be calculated by pressing “Crtl+j” or “Run Replications” (at the bottom of the spreadsheet).

The MS-Excel files create graphs of the univariate and bivariate Markov chain, with and without limits T_{Li} and T_{Ui} being presented, and the prior, likelihood and posterior pdfs of each component concentration. The graph of the bivariate Markov chain shows, in yellow points, the c_i values or vectors that have, at least, one component concentration outside the limits.

The spreadsheets present the number of simulations performed and the number of simulations used to describe the posterior pdf to allow checking the efficiency of the Markov chain process. The burn-in period, the thinning interval and the rejection of each new iteration of the Markov chain reduces the efficiency of the process.

Several tools are available for performing MCMC simulations, such as commercial add-ins of the MS-Excel [21] or free software such as WinBUGS [22] and packages for R programming [23]. However, use of these tools for the risk evaluation in conformity assessment requires some programming skills.

3.1. Validation of spreadsheet calculations

The validation of the spreadsheet calculations was based on the comparison of specific risk estimates with corresponding analytical results, obtained in the R programming environment.

The studied scenarios are those covered in IUPAC Project [5] and briefly described above in Introduction.

Omitting the chemical details already available in the references, Tables 1 to 3 present the studied scenarios and the specific (particular and total) risk estimates performed by means of the different tools. The calculation by the R-software is faster and more accurate than that obtained by the MS-Excel program, but MS-Excel is a more accessible tool and language for most analysts and the program is user friendly, simply requiring the user to set some parameters and choose among a couple of distributional families.

One can find in the tables the means and the standard deviations of 50 MS-Excel estimates of specific risks based on 15000 or 150000 iterations, respectively, allowing understanding the performance of the MCMC. This does not vary significantly, leading to small changes in the parameters of the Markov Chain.

In the studied scenarios, the computational efficiency of the Markov chains, i.e. the percentage of simulations used to describe the posterior distribution, is about 20 % and, therefore, approximately 3000 or 30000 iterations are actually used to reconstruct the posterior pdf when a total number of 15000 or 150000 iterations are performed, respectively. In theory, these numbers of simulations can identify a minimum probability value of 0.03 % or 0.003 % (i.e. frequency 1/3000 or 1/30000, respectively) of false or correct compliance decisions, depending on the kind of discussed specific risk.

The specific risks, estimated for uncorrelated cases by the spreadsheet "UnCorrel4Risk.xlsm" and by the analytical means, are shown in Tables 1 and 2. Table 1 presents results where the prior and the likelihood were both normal [6], Table 2 - where the prior was lognormal, while the likelihood was normal [7].

Table 1

Table 2

Performance of the MS-Excel file "Correl4Risk.xlsm" used for estimation of the specific risks in the case of correlated test results for four material components [8] is shown in Table 3.

Table 3

The MS-Excel files provide also confidence intervals ($R^* \pm k s_{R^*}$) for the specific risk, where R^* and s_{R^*} are the mean and the standard deviation of the risk estimates and k is the quantile of a Student's distribution with 49 degrees of freedom, for 95 % or 99 % level of confidence. In the performed validation, 46 specific risk estimates agree at a 95 % level of confidence with the analytical corresponding values (in the sense that the latter is encompassed in the interval), whereas only 4 cases agree at a 99 % level of confidence. Similar results were

obtained in the case described in ref. [10]. It can be concluded that the risk estimates from the MS-Excel files are in good agreement with the analytical results. The standard deviations of the risk estimates ranged from 0.001 % to 1.5 %, depending of the specific risk value. Since 95 % level of confidence is applied in the majority of measurements in chemistry, it can be concluded that the performance of the developed MS-Excel files is adequate to distinguish cases where the specific risk is too large or acceptably low. If more accurate risk estimates are required, the analytical tools and R programming should be used [5-8, 10].

4. Conclusions

The principles of Bayesian inference are discussed in a simple but comprehensive way allowing correct formulation of a scenario involved in determination of specific risks (particular and total) of false decisions in conformity assessment of a multicomponent material or object.

A tutorial and two user-friendly MS-Excel spreadsheets are presented based on the Markov Chain Monte Carlo Method using the Metropolis–Hastings algorithm (MCMC-MH). The spreadsheets provide easy, fast and adequately accurate estimates of the risks. The principles of the MCMC-MH are also explained shortly, as necessary for a suitable choice of Markov Chain parameters.

There is a good agreement between the results estimated by means of the developed spreadsheets and the results obtained analytically in R programming environment.

The MS-Excel platform has the advantage easy linking the developed files with other spreadsheets, where complex measurement uncertainty models and/or concentration constraints may be implemented as the input information of Bayesian inference.

The developed tutorial and the spreadsheets can be helpful in different conformity assessment tasks related to multicomponent materials or objects.

Electronic supplementary material

- File to process values with negligible correlation: UnCorrel4Risk.xlsm
- Video explaining the use of the file UnCorrel4Risk.xlsm: Demo_UnCorrel4Risk.mp4
- File to process correlated values: Correl4Risk.xlsm
- Video explaining the use of the file Correl4Risk.xlsm: Demo_Correl4Risk.mp4

Acknowledgment

This research was supported in part by the International Union of Pure and Applied Chemistry (IUPAC Project 2016-007-1-500).

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Figure captions

Fig. 1. Starting point for MCMC calculation. a) Lognormal prior pdf and a starting point $c_i = \alpha$ with probability density $p(\alpha)$; and b) Gaussian (normal) likelihood and a starting point $c_i = \alpha$ with probability density $p(c_{im} \mid \alpha)$.

Fig. 2. Dependence of the sampled c_i value on the number of iterations in MCMC simulations with Metropolis–Hastings algorithm at different increment sizes *t*. a) A small *t* does not allow to reach the mode of $p(c_i|c_{im})$; b) a large *t* reduces the number of iterations of sampling $p(c_i|c_{im})$, but produces a weaker description of the distribution; and c) adequate *t* value leads to a noisy line of c_i values vs. the number of iterations. The blue circle indicates the starting point α.

Fig. 3. Variations of the sampled vector c_{12} with the number of iterations in MCMC simulations using Metropolis–Hastings algorithm at different vectors *t* of the increment sizes. a) Small modulus vector $\boldsymbol{t}_{12}$ and a starting point (blue circle) away from the mode of the bivariate distribution; b) a large modulus vector $\boldsymbol{t}_{12}$; and c) an adequate vector $\boldsymbol{t}_{12}$, where the burn-in period should be increased to remove the tail of points between the starting point and the bivariate distribution.

Table 1. Comparison of the specific total consumer's risk $R^*_{\mathbf{total(c)}}$ (%) in the conformity assessment of denatured alcohols, when from one to three denaturant concentrations are tested

#	Prior	Likelihood	T_{Li}		Analytical	MS-Excel (UnCorrel4Risk.xlsm)	
1	Normal	Normal		c_m	$R^*_{c1(c)}$	$\bar{R}^*_{c1(c)}$ (I=15000)§	$\bar{R}^*_{c1(c)}$ (I=150000)§
	μ = 3.15; σ = 0.1575	c_m (see corresponding column on the right); u = 0.05	T_L = 3	3	38.66	37.8; 1.5	38.04; 0.46
				3.08	3.490	3.20; 0.37	3.21; 0.11
				3.15	0.0823	0.062; 0.056	0.068; 0.018
				3.22	0.000370	0.0003; 0.0028	0.0003; 0.0011
				3.3	1×10^{-7}	< 0.03 †	< 0.003 †
2	Normal	Normal			5.9	5.41; 0.62	5.40; 0.20
	μ_1 = 3.15; σ_1 = 0.1575	c_{1m} = 3.10; u_1 = 0.05	T_{L1} = 3				
	μ_2 = 3.15; σ_2 = 0.1575	c_{2m} = 3.10; u_2 = 0.07	T_{L2} = 3				
3	Normal	Normal			18.8	18.3; 1.2	18.3; 0.37
	μ_1 = 3.15; σ_1 = 0.1575	c_{1m} = 3.10; u_1 = 0.05	T_{L1} = 3				
	μ_2 = 3.15; σ_2 = 0.1575	c_{2m} = 3.10; u_2 = 0.07	T_{L2} = 3				
	μ_3 = 1.10; σ_3 = 0.11	c_{3m} = 1.05; u_3 = 0.07	T_{L3} = 1				

Notes. Estimates from the analytical solution [6] and the numerical MCMC implemented in the developed MS-Excel file 'UnCorrel4Risk.xlsm'. In the presented examples both the prior pdf and the likelihood are normal, and the test results are not correlated.
T_{Li} – lower legal limit; I – number of iterations; § – mean value; standard deviation; † – the reverse of the number of simulation used to describe the posterior pdf, i.e. about 20 % of all performed simulations.

Table 2. Comparison of the specific total consumer's risk $R^*_{\mathbf{total(c)}}$ (%) in the conformity assessment of total suspended particulate matter concentration in air near one to three stone quarries

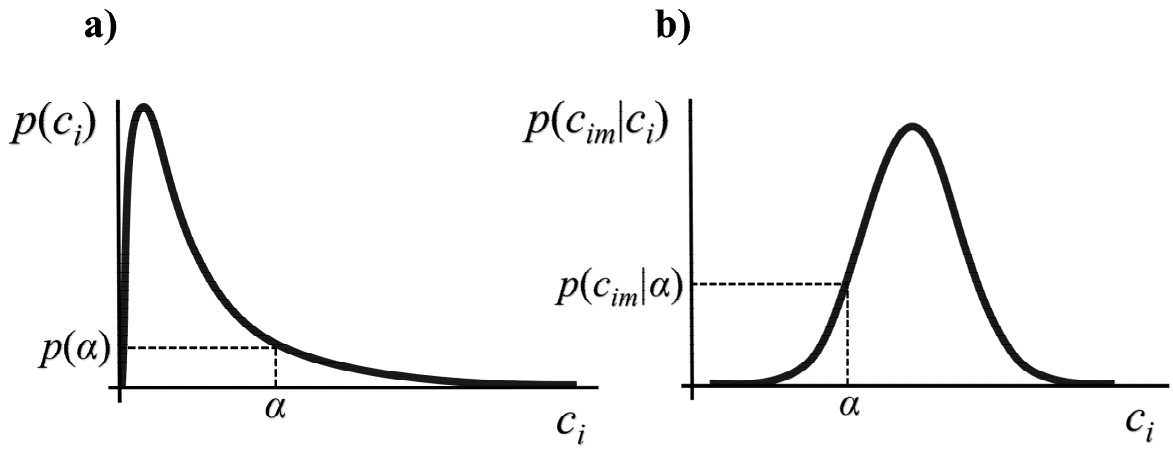
#	Prior	Likelihood	T_{Ui}		Analytical	MS-Excel (UnCorrel4Risk.xlsm)	
1	Lognormal	Normal		c_m	$R^*_{c1(c)}$	$\bar{R}^*_{c1(c)}$ (I=15000)§	$\bar{R}^*_{c1(c)}$ (I=150000)§
	μ = -2.326; σ = 0.434	c_m (see corresponding	T_U = 0.2	0.161	0.00817	0.010; 0.017	0.0075; 0.0049
		column on the		0.167	0.0840	0.088; 0.057	0.079; 0.019
		right); $u = 0.07c_m$		0.175	0.884	0.86; 0.19	0.839; 0.061
				0.187	8.96	8.68; 0.70	8.75; 0.22
				0.200	35.5	36.2; 1.2	36.21; 0.38
2	Lognormal	Normal	T_{Ui} = 0.2		54.86	56.4; 1.2	56.29; 0.62
	μ_1 = -2.031; σ_1 = 0.280	c_{1m} = 0.2; c_{2m} = 0.2					
	μ_2 = -2.338; σ_2 = 0.403	$u_i = 0.07c_{im}$					
3	Lognormal	Normal	T_{Ui} = 0.2		32.81	34.5; 1.4	34.6; 0.73
	μ_1 = -2.326; σ_1 = 0.434	c_{1m} = 0.194; c_{2m} = 0.192					
	μ_2 = -2.031; σ_2 = 0.280	c_{3m} = 0.114					
	μ_3 = -2.338; σ_3 = 0.403	$u_i = 0.07c_{im}$					

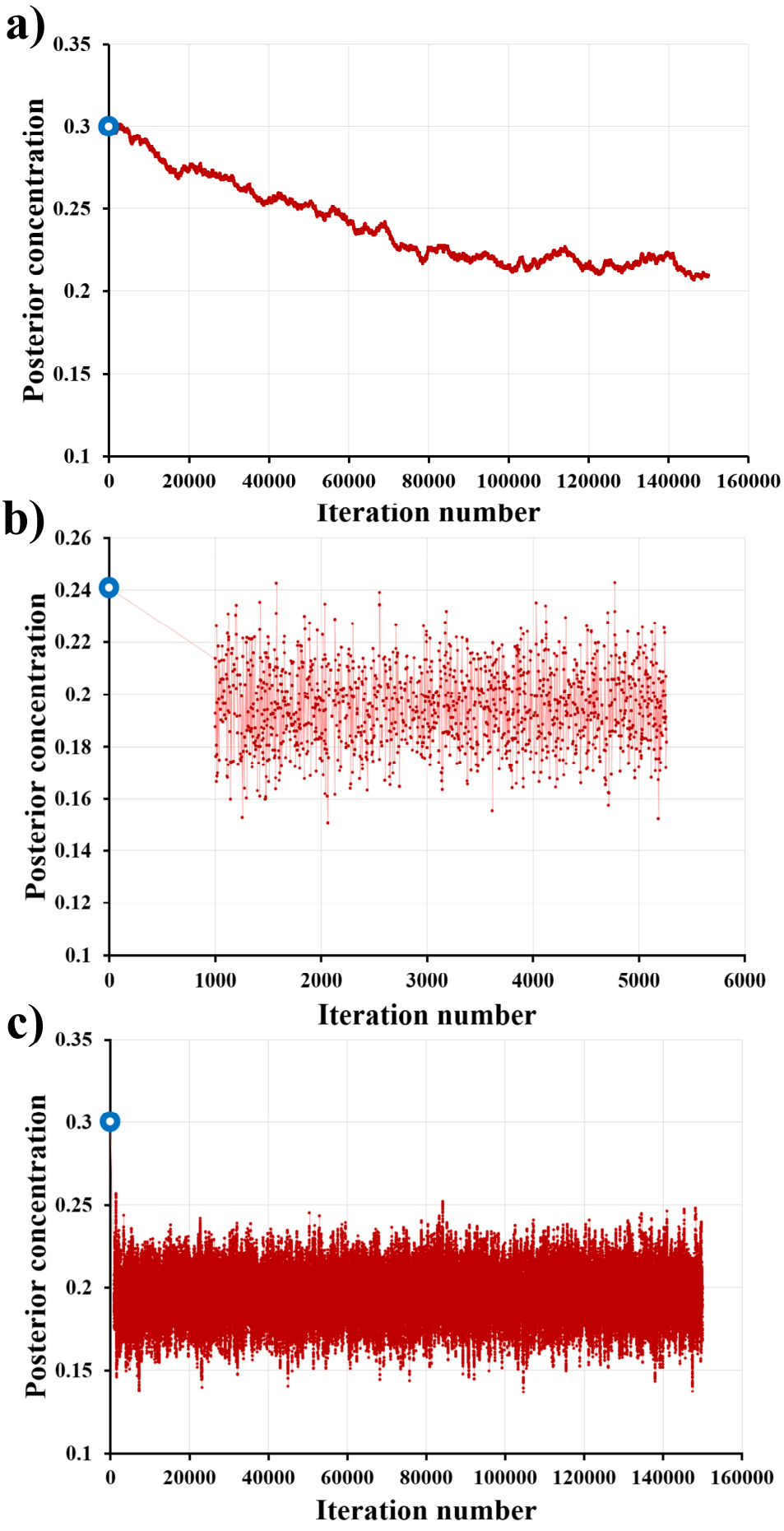
Notes. Estimates from the analytical solution [7] and the numerical MCMC implemented in the developed MS-Excel file 'UnCorrel4Risk.xlsm'.
In the presented examples, the prior pdf and the likelihood are lognormal and normal, respectively; the test results are not correlated.
T_{Ui} – upper legal limit; I – number of iterations; § – mean value; standard deviation.

Table 3. Comparison of the specific total consumer's risk $R^{*}_{\mathbf{total(c)}}$ (%) in conformity assessment of a medicine with four active components

#	Prior	Likelihood	$[T_{\mathrm{L}i}, T_{\mathrm{U}i}]$	Analytical		MS-Excel (Correl4Risk.xlsm)	
1	Normal	Normal		c_{1m}	$R^{*}_{\mathrm{total(c)}}$	$\bar{R}^{*}_{\mathrm{total(c)}}$ (I=15000)§	$\bar{R}^{*}_{\mathrm{total(c)}}$ (I=150000)§
	μ_1 = 99.18; σ_1 = 1.37	c_{1m} (see relevant column);	[95, 105]	95	0.600	0.58; 0.24	0.569; 0.071
	μ_2 = 97.7; σ_2 = 1.02	u_1 = 0.028 c_{1m};		97.5	0.344	0.33; 0.16	0.329; 0.053
	μ_3 = 99.33; σ_3 = 1.05	c_{2m} = 97.7; u_2 = 2.74;		100	0.274	0.27; 0.14	0.261; 0.046
	μ_4 = 98.94; σ_4 = 1.22	c_{3m} = 99.33; u_3 = 2.78;		102.5	0.257	0.26; 0.15	0.246; 0.041
	Correlation coefficients	c_{4m} = 98.94; u_4 = 2.77		105	0.255	0.24; 0.11	0.238; 0.045
	r_{12}=0.107; r_{13}=0.125;	Correlation coefficients					
	r_{14}=0.177; r_{23}=0.311;	*(see Prior)*					
	r_{24}=0.404; r_{34}=0.539						
2	Normal	Normal		c_{1m}	$R^{*}_{\mathrm{total(c)}}$	$\bar{R}^{*}_{\mathrm{total(c)}}$ (I=15000)§	$\bar{R}^{*}_{\mathrm{total(c)}}$ (I=150000)§
	As in case 1	*As in case 1*	[95, 105]	95	0.591	0.56; 0.21	0.563; 0.066
	Correlation coefficients	Correlation coefficients		97.5	0.342	0.32; 0.16	0.326; 0.049
	Negligible	*Negligible*		100	0.279	0.28; 0.12	0.257; 0.037
				102.5	0.264	0.24; 0.12	0.246; 0.037
				105	0.265	0.28; 0.15	0.246; 0.041

Notes. Estimates from the analytical solution [8] and the numerical MCMC implemented in the developed MS-Excel file 'Correl4Risk.xlsm'. In the presented examples the prior pdf and the likelihood are normal; the test results of the component concentrations are correlated. $T_{\mathrm{L}i}$ and $T_{\mathrm{U}i}$ – lower and upper specification limits; I – number of iterations; § – mean value; standard deviation.




a)
Posterior concentration
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0.3
0.25
0.2
0.15
0.1
0
20000
40000
60000
80000
100000
120000
140000
160000
Iteration number
b)
Posterior concentration
0.26
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0
1000
2000
3000
4000
5000
6000
Iteration number
c)
Posterior concentration
0.35
0.3
0.25
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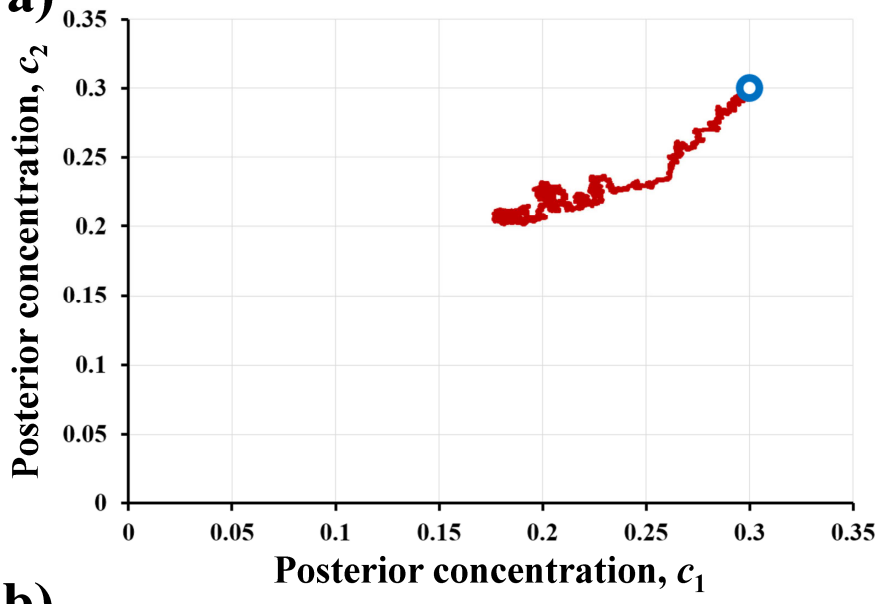
100000
120000
140000
160000
Iteration number

a)


Posterior concentration, c_2
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0.2
0.15
0.1
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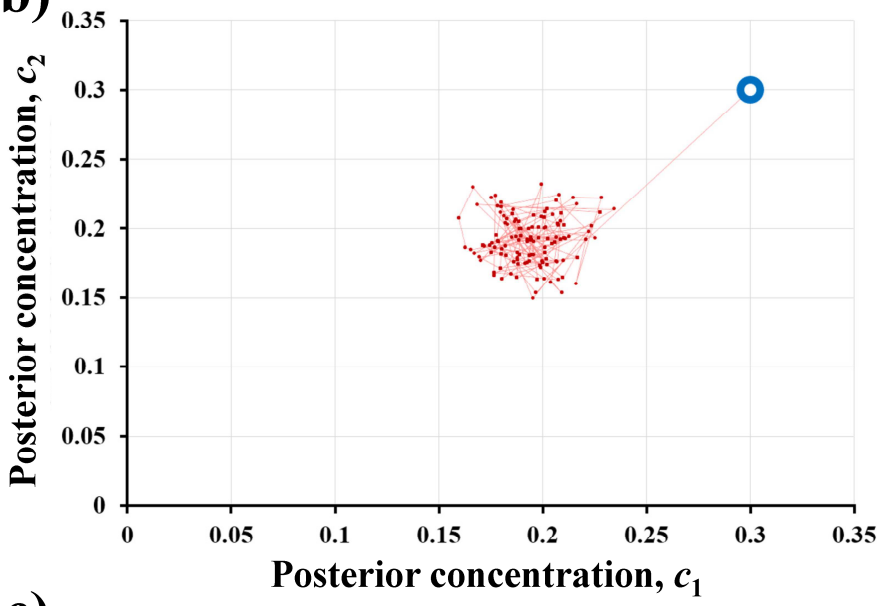
0.1
0.15
0.2
0.25
0.3
0.35
Posterior concentration, c_1

b)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0.25
0.2
0.15
0.1
0.05
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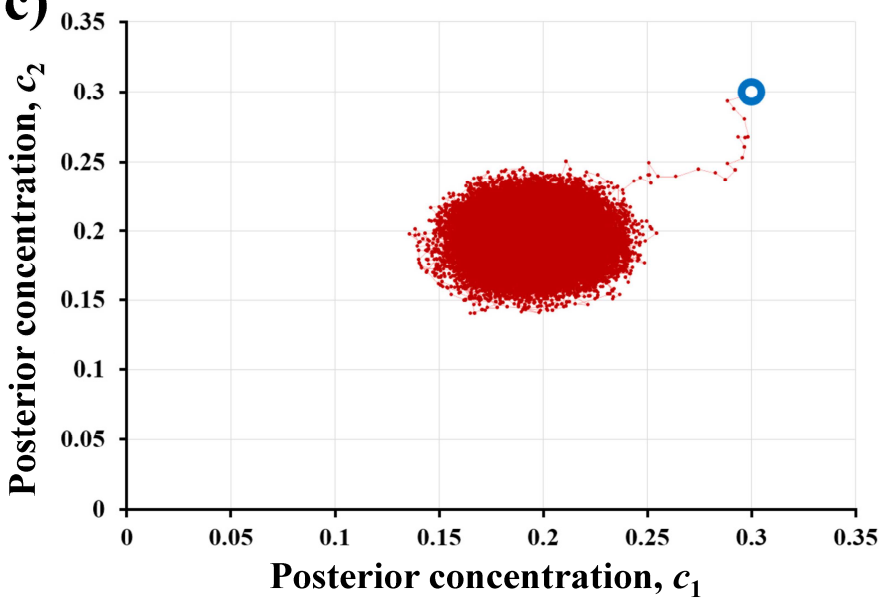
0.15
0.2
0.25
0.3
0.35
Posterior concentration, c_1

c)


Posterior concentration, c_2
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0.3
0.25
0.2
0.15
0.1
0.05
0
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
Posterior concentration, c_1

HIGHLIGHTS

- A tutorial and MS-Excel spreadsheets for evaluating risks of false decisions in conformity assessment of a multicomponent material are presented.
- The developed program is based on Bayesian approach and Markov Chain Monte Carlo (MCMC) simulations by the Metropolis-Hastings algorithm.
- The principles of Bayesian inference and MCMC are described for analytical chemists with basic knowledge in statistics.
- The program was validated by comparison of the obtained results with the results calculated in R programming environment.
- The spreadsheets and audio-video instructions explaining the program use are provided as electronic supplements.