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PRACTITIONER'S REPORT

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A software package comparison for uncertainty measurement estimation according to GUM

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Abstract Six commercial programs devoted to the estimation of measurement uncertainty were compared for feasibility in order to be applied in routine chemical analysis. The main features of each program were discussed. They were applied to two well-documented case studies. Several screen captures were considered for illustration.

Keywords Measurement uncertainty · GUM approach · Monte-Carlo simulation

Introduction

Measurement uncertainty is the most important criterion in both method validation and internal quality control [1]. The increasing implementation of accreditation and quality control pinpoints the need of suitable approaches to estimate the measurement uncertainty. This is reflected in the accreditation standard EN-ISO/IEC 17025 whose clause 5.4.6.2 states that "Testing laboratories shall have and shall apply procedures for estimating uncertainty of measurement". A sound and well-established approach for evaluating the measurement uncertainty is set out in the "Guide to the expression of Uncertainty Measurement" (GUM) [2–3] and several reputed organizations recommend its application [4]. However, it is also clear that GUM approach encompasses a tedious and error-prone series of calculations and accordingly, laboratory managers are aware of the benefits of using a software package to perform GUM calculations. Rasmussen [5] reviewed the software tools for the expression of uncertainty in measurement from the viewpoint of supporting testing laboratories. The aim of the present paper is beyond this goal and it deals with the comparison of some of the widely used software packages for GUM estimation of measurement uncertainty. The comparison is made on the basis of user-friendly features and facilities for laboratory personnel. Also, taking into account that the first supplemental guide to the current GUM edition deals with the propagation of distributions and emphasizes the use of Monte-Carlo simulation for measurement uncertainty, some programs performing it were chosen.

Demos or evaluation versions of the following software tools have been selected for comparison: Assistant [6], GUM Workbench [7], Uncertainty Pro [8], Crystal Ball [9], Decision Pro [10] and @Risk [11]. The first three perform classical GUM evaluation of measurement uncertainty and the last three enable us to apply the Monte-Carlo approach. In order to carry out the comparison, two case studies were selected. The first one is quoted from the EURACHEM/CITAC guide [3]: example A1: preparation of a calibration standard (pp 34–39) yet discussed in [4]. The second one is quoted from Yang and Willie [12] and deals with the determination of lead in tap water by atomic absorption spectrometry [13].

Worked example 1: preparation of a calibration standard

The explanation has been quoted from [4]. The goal is to prepare a calibration standard of high purity cadmium with a concentration of ca. 1000 mg/l. The measurand is the concentration of standard solution, which depends upon the weighing of the high purity metal (Cd), its purity, and the volume of the liquid in which is dissolved.

According to GUM the following stages are considered:

(1) *Specification step:* The model equation is

$$C = \frac{1000 m P}{V} \tag{1}$$

where C is the concentration of the standard (mg/l), m the mass of high purity cadmium dissolved (mg), P the purity and V the volume of the final solution (ml). The scale factor 1000 is used to convert ml to l.

(2) *Identification step:* The sources of significant uncertainty for each parameter affecting the measurand are:

Table 1 Combined uncertainty obtained by the six programs for the two worked examples selected

Software	Worked example 1	Worked example 2
Assistant	0.833	0.633
GUM Workbench	0.838	0.633
Uncertainty Pro	0.835	0.638
Crystal Ball	0.833	0.633
Decision Pro	0.835	0.635
@Risk	0.838	0.633

Purity, P: The purity of the metal (Cd) is quoted in the supplier's certificate as 99.99±0.01%. P is therefore 0.9999±0.0001. These values depend on the effectiveness of the surface cleaning of the high purity metal.

Mass, m: This involves weighing the high purity metal. A 100-ml quantity of a 1000 mg/l cadmium solution is to be prepared. The mass of cadmium is determined by a tared weighing, giving m=0.10028 g.

Volume V: The volume of the solution contained in the volumetric flask is subject to three major sources of uncertainty: the uncertainty in the certified internal volume of the flask, the variation in filling the flask to the mark,

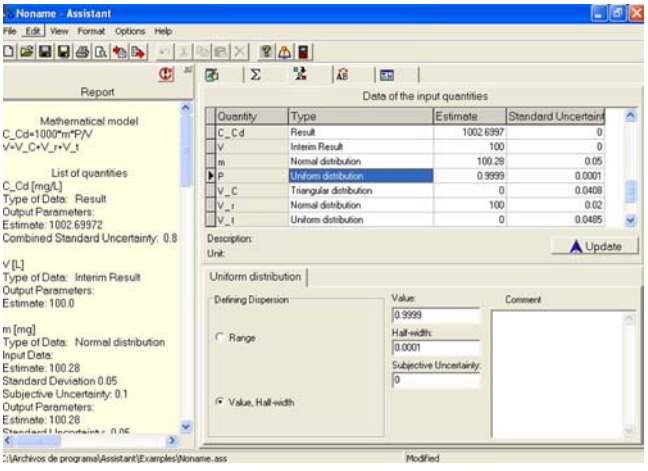


Fig. 1 Introduction of input data in Assistant

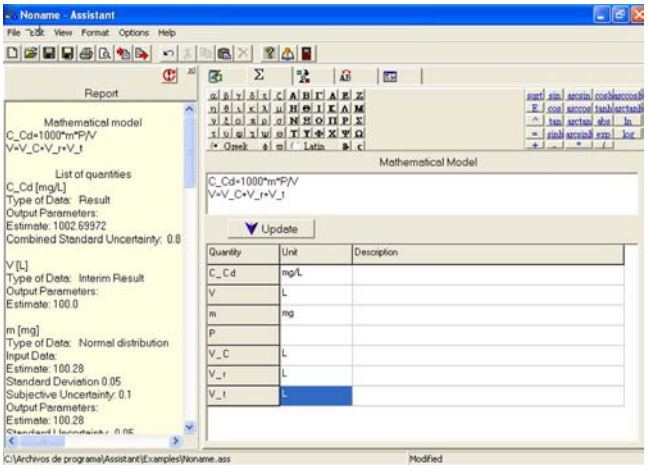


Fig. 2 Building of the measurand and interim model in Assistant

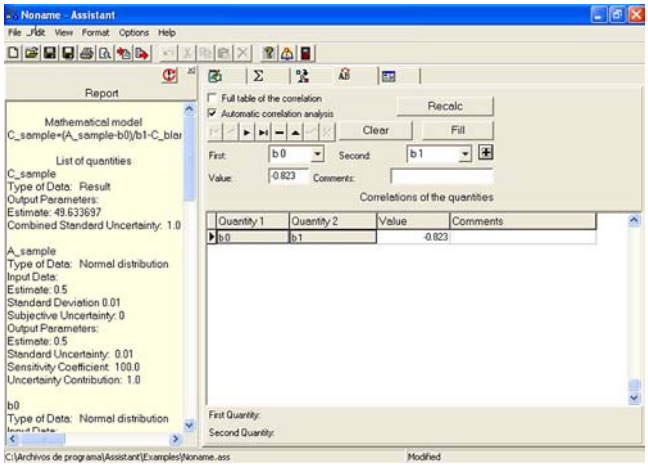


Fig. 3 Consideration of the correlation between variables b_0 and b_1

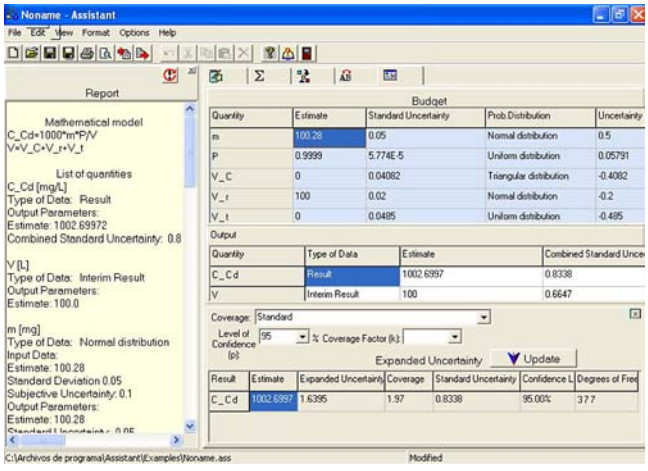


Fig. 4 Final results produced by Assistant

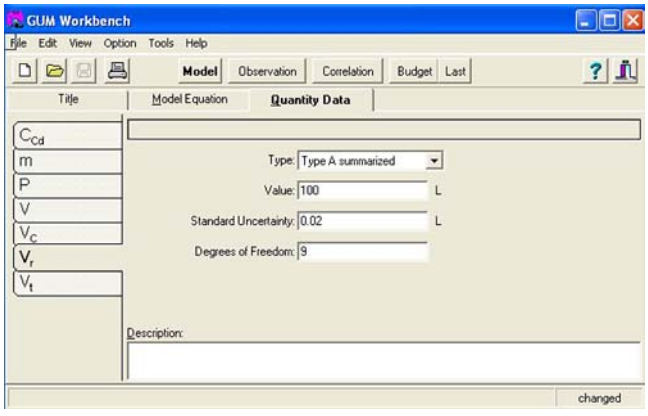


Fig. 5 Data introduction in GUM Workbench

and the flask and solution temperatures differing from the temperature at which the volume of the flask was calibrated.

(3) *Quantification step:* The different uncertainties are calculated as follows:

Purity, P: The purity of the cadmium is given on the certificate as 0.9999±0.0001. Thus, it is a type B uncertainty.

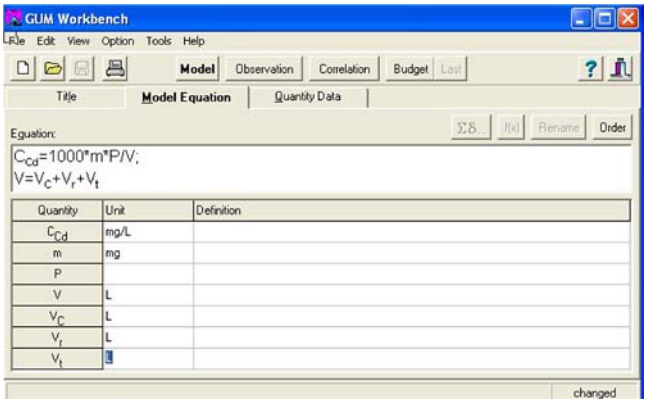


Fig. 6 Equation models in GUM Workbench

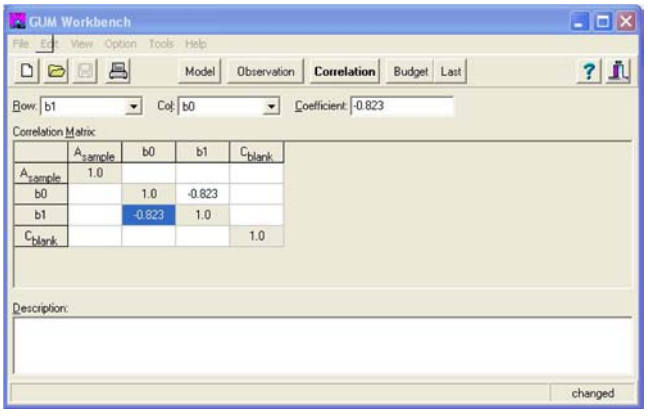


Fig. 7 Correlation introduction in GUM Workbench as a matrix

Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Sensitivity Coefficient	Uncertainty Contribution
m	100.2800 mg	0.0500 mg	50	10	0.50 mg/L
P	0.9999000	0.0000577	infinity	1000	0.058 mg/L
V	100.0000 L	0.0665 L			
V_C	0.0 L	0.0408 L	infinity	-10	-0.41 mg/L
V_r	100.0000 L	0.0200 L	9	-10	-0.20 mg/L
V_t	0.0 L	0.0485 L	infinity	-10	-0.49 mg/L
C_{Cd}	1002.70 mg/L	0.835 mg/L	340		

Result: Quantity: C_{Cd}
Value: 1002.7 mg/L
Expanded Uncertainty: ±1.7 mg/L
Coverage Factor: 2.0
Coverage: t-table 95%

Fig. 8 Output generated by GUM Workbench

Because there is no additional information about the uncertainty value, a rectangular distribution is assumed. To obtain the standard uncertainty $u(P)$ the value of 0.0001 has to be divided by $\sqrt{3}$:

$$u(P) = \frac{0.0001}{\sqrt{3}} = 0.0000577$$

Mass, m: The uncertainty associated with the mass of the cadmium is estimated, using the data from the calibration certificate and the manufacturer's recommendations on uncertainty estimation, is $u(m) = 0.05$ mg. This is a type B uncertainty and it is assumed a normal distribution.

Volume, V: The volume has three major influences; calibration, repeatability and temperature effects that can be split into three contributions: V_{cal}, V_{rep} and V_{temp}.

i) *Calibration* (V_{cal})*:* The manufacturer quotes a volume for the flask of 100 ml ± 0.1 ml measured at a temperature of 20°C. The value of the uncertainty is given without confidence level or distribution information, so an assumption is necessary. Here, the standard uncertainty is calculated as a type B one, assuming a triangular distribution, and $u(V_{\text{cal}})$ is obtained by dividing 0.1 by $\sqrt{6}$:

$$u(V_{\text{cal}}) = \frac{0.1}{\sqrt{6}} = 0.0408$$

ii) *Repeatability* (V_{rep}): The uncertainty due to variations in filling can be estimated as a type A uncertainty from a repeatability experiment on a typical example of the flask used. A series of 10 fill and weigh experiments in a typical 100 ml flask gave a standard deviation of 0.02 ml. This can be used directly as a standard uncertainty. Thus, $u(V_{\text{rep}})$=0.02

iii) *Temperature* (V_{temp}): According to the manufacturer, the flask has been calibrated at a temperature of 20°C, whereas the laboratory temperature varies between the limits of ±4°C. The type B uncertainty from this effect can be calculated from the estimate of the temperature range and the coefficient of the volume expansion. The volume expansion of the liquid is considerably larger than that of the flask, so only the former needs to be considered. The coefficient of volume expansion for water is 2.1×10^{-4} °C^{-1}, which leads to a volume variation of $\pm(100\times4\times2.1\times10^{-4})=\pm0.084$ ml. The standard uncertainty is calculated using the assumption of a rectangular distribution for the temperature variation:

$$u(V_{\text{temp}}) = \frac{0.084}{\sqrt{3}} = 0.0485$$

The volume V can be considered as an interim result with an interim model equation

$$V = V_{\text{cal}} + V_{\text{rep}} + V_{\text{temp}} \tag{2}$$

The expected value of V must be calculated also from Eq. 2, and therefore the value of 100 ml can be ascribed only to one of the three terms. It seems to be advisable to assign the value 100 ml to the expectation of V_{rep} (because this value was obtained by a series of 10 measurements with a standard deviation of 0.02) and to take zero for the expectations of both V_{cal} and V_{temp}. Accordingly, the expected value of V from Eq. 2 will be: V=100+0+0=100 ml, and

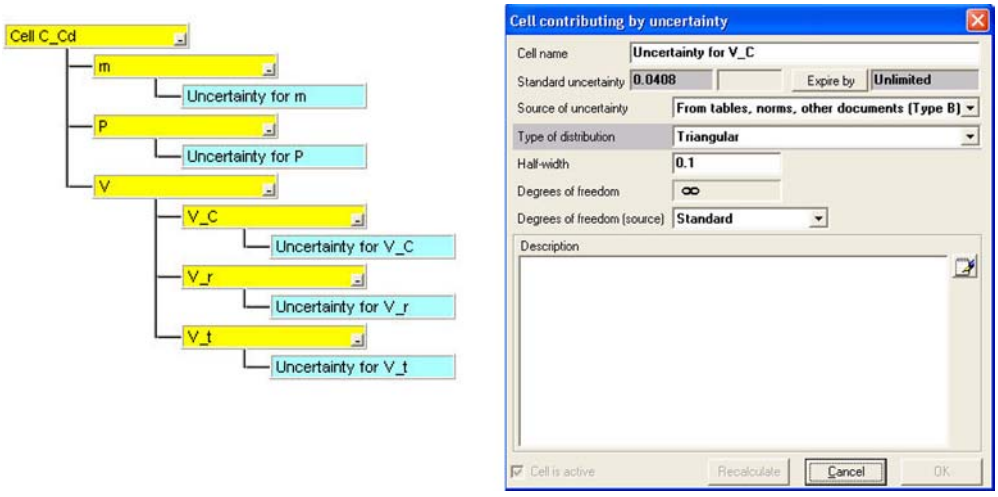


Fig. 9 Data introduction by using the variable tree and clicking the variable cell in Uncertainty Pro

the interim combined standard uncertainty $u(V)$ of the volume V:

$$u(V) = \sqrt{u^2(V_{\text{cal}}) + u^2(V_{\text{rep}}) + u^2(V_{\text{temp}})} = 0.0665$$

(4) *Calculation of the combined standard uncertainty of C*: By applying the law of error propagation to Eq. 1 after evaluating partial derivatives we get:

$$u(C) = \sqrt{\left(\frac{1000P}{V}\right)^2 u^2(m) + \left(\frac{1000m}{V}\right)^2 u^2(P) + \left(-\frac{1000mP}{V^2}\right)^2 u^2(V)}$$

that yields to the value of the combined uncertainty $u(C)$=0.8354.

The computation of the expanded standard uncertainty can be obtained upon normality assumption for about the 95% confidence level using a coverage factor k=2: $u(C)$=1.6708, but some other possibilities are available. The use of the Student tabulated value as coverage factor is more advisable is some cases.

Monte-Carlo analysis

In our example, the model equation (and the interim one) has been set already, and the sources of uncertainty, identified. The selection of the probability density functions for the different parameters can be done from the information gathered in Table 1. Thus, P is a random variable uniformly distributed with expectation 0.9999 and range 0.9998–1.0000, m is normally distributed with mean 100.28 and standard deviation 0.05, V_{cal} follows a triangular distribution with zero mean and interval ± 0.1, V_{rep} can be assumed to follow a normal distribution with expectation 100 and standard deviation 0.02, and finally, V_{temp} is uniformly distributed with zero mean and interval ± 0.084.

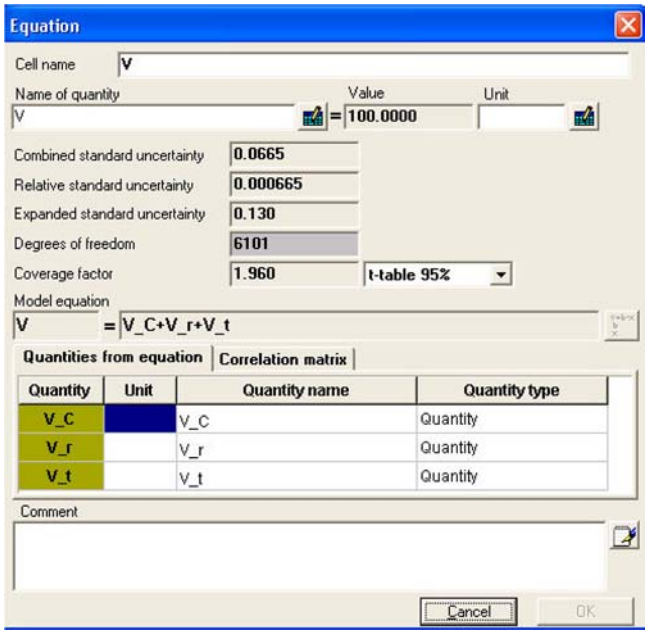


Fig. 10 Model equation building with Uncertainty Pro

Monte-Carlo simulation with 100000 trials was selected. From the report, the following data were quoted:

- Mean value: 1002.6985
- Median: 1002.6968
- Standard deviation: 0.8348
- Skewness: −0.0030
- Confidence interval for 95%: [1001.0760, 1004.3245]

The comparison of the results for combined uncertainty obtained by using both approaches did not show any significant difference.

Worked example 2: uncertainty in the determination of lead in a tap water by atomic absorption spectrometry

This explanation is quoted from [13] and deals with the determination of lead in tap water from atomic absorption

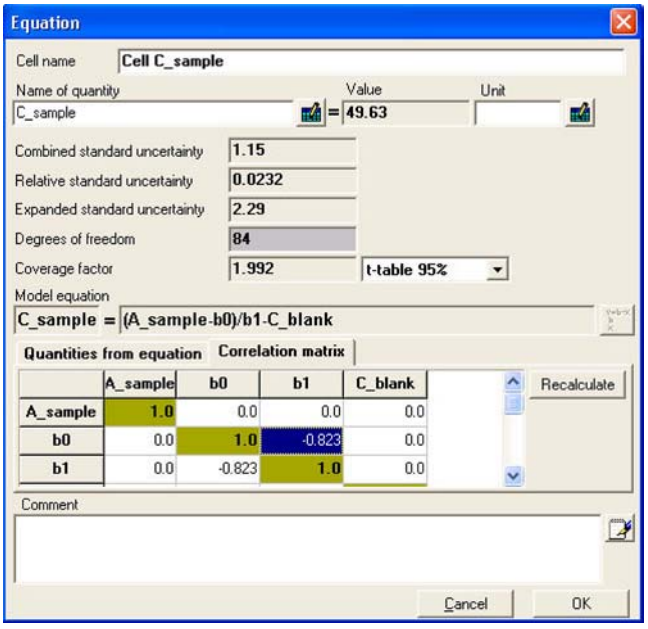


Fig. 11 Introduction of the correlation between variables as a matrix in Uncertainty Pro

spectrometry using an external calibration curve. If A stands for the absorbance values and C stands for the concentration of Pb, the following linear relationship is obtained:

$$A = b_0 + b_1 C \tag{3}$$

The intercept, b_0=−0.000377, has a standard uncertainty $u(b_0)$=0.004424 and the slope, b_1=0.0100008, has a standard a standard uncertainty $u(b_1)$=0.00006827. Both parameters b_0 and b_1 are correlated with a correlation coefficient obtained from

$$r(b_0, b_1) = -\frac{\sum_{i=1}^{N} C_i \; u(b_1)}{N \; u(b_0)} \tag{4}$$

N being the number of points, leading to $r(b_0,b_1)$= −0.8230.

A tap water sample was measured in triplicate, giving the absorbance values: 0.500, 0.505 and 0.495. The blank concentration expressed as Pb in ng/g was estimated in three separated experiments leading to 0.40, 0.30 and 0.50 ng/g. The concentration of Pb in the sample is obtained from the model:

$$Z = \frac{A_{\text{sample}} - b_0}{b_1} - C_{\text{blank}} \tag{5}$$

Assuming that all input parameters are normally distributed, we operate as follows:

C_{blank} is a random variable normally distributed with expectation 0.40 ng/g and standard deviation 0.10 ng/g, A_{sample} is normally distributed with mean 0.500 and standard deviation 0.010, b_0 follows also the Gauss distribution with mean −0.000377 and standard deviation 0.004424, and finally, b_1 is also normally distributed with 0.0100008 mean and standard deviation 0.00006827.

The GUM steps (1)–(4) leads to a combined uncertainty $u(Z)$=0.632. By performing a Monte-Carlo simulation with 100000 trials, the results were:

- Mean value: 49.635 ng/g
- Median: 49.636 ng/g
- Standard deviation: 0.633 ng/g
- Skewness: −0.0067
- Confidence interval for 95%: [48.39273, 50.87563]

As can be observed, in this case, results from both approaches agree well, mainly due to the more linear model and the assumption that all input parameters have a normal PDF.

Results and discussion

The six commercial programs selected were applied to these two examples. The results obtained are gathered in Table 1. As it can be observed, the uncertainties calculated with the different programs present differences in the last (third) digit. The uncertainty of measurements is essential to report the correct number of significant figures of the result. In fact, the first significant figure of the uncertainty is the first uncertain figure of the average result, and consequently, its final significant figure. Thus, it seems to be immaterial the found variability in the third decimal place of the uncertainty. Anyway, the source of this variability can be explained as follows.

Programs using Monte-Carlo approach perform simulated samples of the measurand, according to the distribution functions of the input variables. The final result are the mean values and standard deviations that come from different simulated samples in each run and accordingly, some slight variability can be expected.

On the other hand, the classical GUM evaluation use partial derivatives to calculate the sensitive coefficients when error propagation is performed, the software tools that perform classical GUM evaluation may use different algorithms (whose source code is not available) to calculate this coefficient, and then, is possible to find some little differences in the computed combined uncertainty.

Accordingly all these studied programs could be used for estimating the uncertainty measurement in routine analysis. However, some of them could be more user-friendly for lab technicians. In the following we will consider the main features of these programs as well as several captures illustrating the way of data input, model equation building, reports and outputs, etc.

Assistant

This program is very systematic, intuitive and straightforward to handle. These features make it very useful to beginners in the manipulation of spreadsheets. The help

Equations:

C_Cd = 1000*m*P/V
V = V_C+V_r+V_t

List of quantities:

Quantity	Unit	Name of quantity
C_Cd		C_Cd
m		m
P		P
V		V
V_C		V_C
V_r		V_r
V_t		V_t

Uncertainty budget:

Quantity	Value	Std. uncertainty	Deg. of freedom	Sensitivity coeff.	Uncertainty contrib.
C_Cd	1002.700	0.835	380		
m	100.2800	0.0500	50	10.0	0.5 %
P	0.9999000	0.0000577	∞	1000	0.1 %
V	100.0000	0.0665	6101		
V_C	0	0.0408	∞	10.0	-0.4 %
V_r	100.0000	0.0200	50	10.0	-0.2 %
V_t	0	0.0485	∞	10.0	-0.5 %

Result:

Quantity	C_Cd
Value	1002.700
Combined standard uncertainty	0.835
Expanded standard uncertainty	±1.64
Coverage factor	1.96
Confidence level	95%

Fig. 12 Presentation of output results in Uncertainty Pro

is a bit Spartan but has a lot of examples for illustration. Data introduction is shown in Fig. 1. The built of the model equations is presented in Fig. 2. The consideration of correlated variables is illustrated in Fig. 3 and the produced results are gathered in Fig. 4.

GUM Workbench

Like Assistant, this is very intuitive, easy and systematic. Practically there is no need of help for performing calcu-

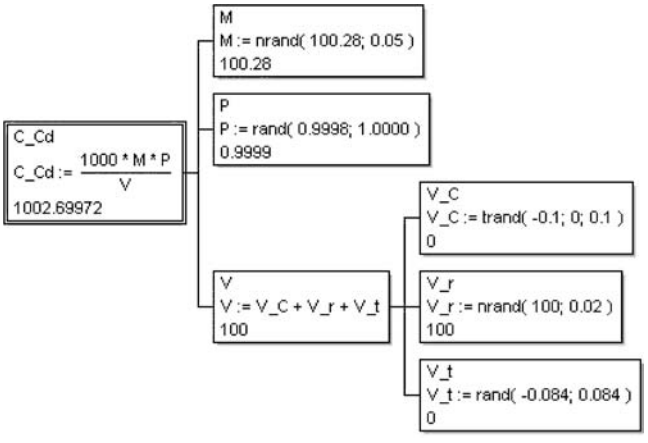


Fig. 13 Data introduction using the variable tree of Decision Pro

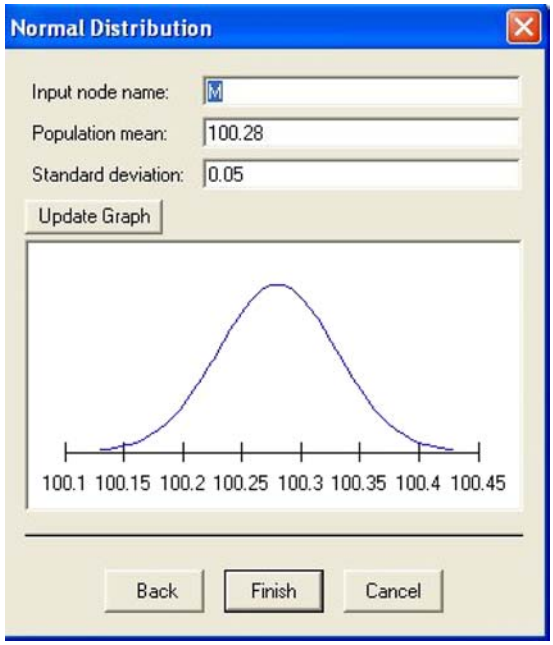


Fig. 14 Distribution selection for input variables in Decision Pro

lations. Anyway the manual is splendid for learning. As in the above considerations, the screen captures showing the data introduction, model equation writing, correlation inclusion and final output correspond to Figs. 5–8.

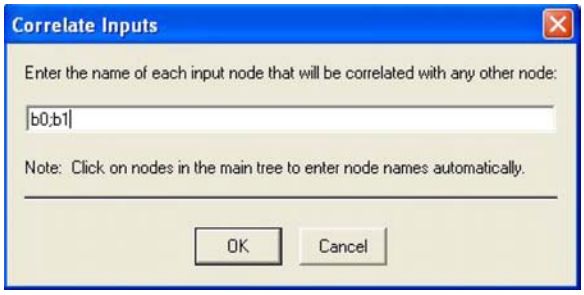


Fig. 15 Introduction of correlation between variables (nodes) in Decision Pro

Simulation Summary

Measure	*C_Cd*
Observations	100,000
Mean	1,002.69448
Standard Deviation	0.83537
Posterior STD	0.00264
Variance	0.69784
Minimum	999.6612
5th Percentile	1,001.31208
Median	1,002.69529
95th Percentile	1,004.06455
Maximum	1,005.63032

Fig. 16 Final output in Decision Pro

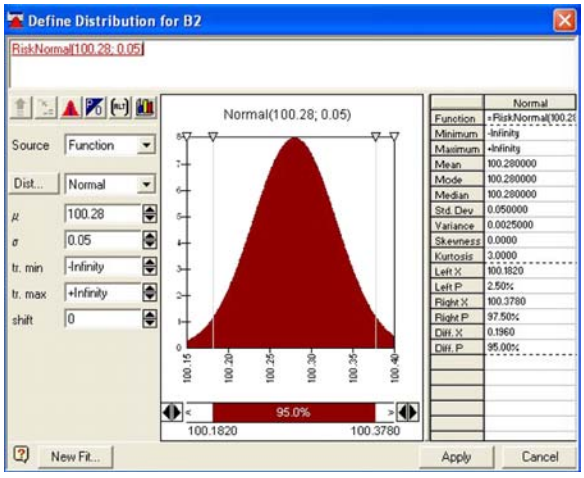


Fig. 17 Definition of distribution features for input variables in @Risk

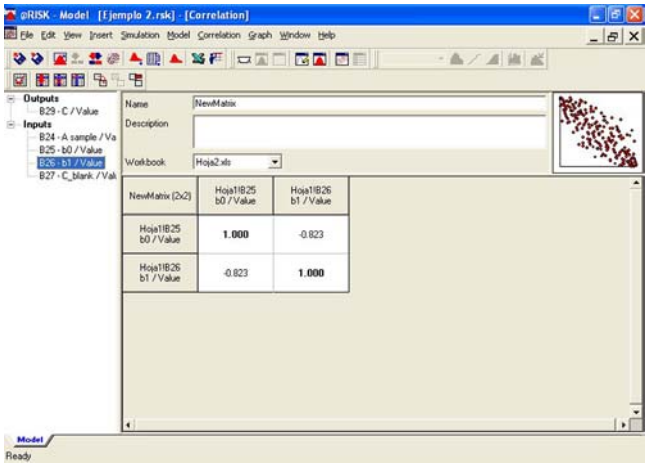


Fig. 18 Introduction of the correlation between variables as a matrix in @Risk

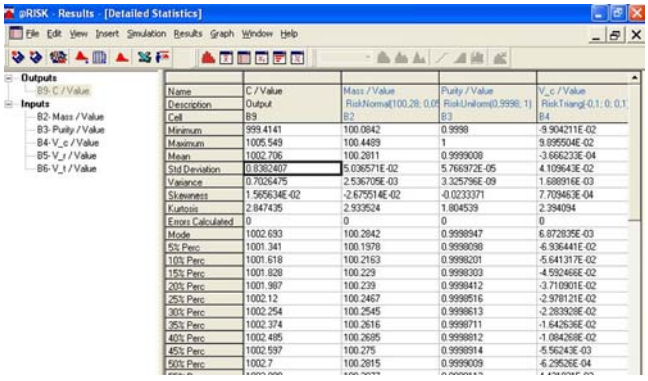


Fig. 19 Final output for @Risk

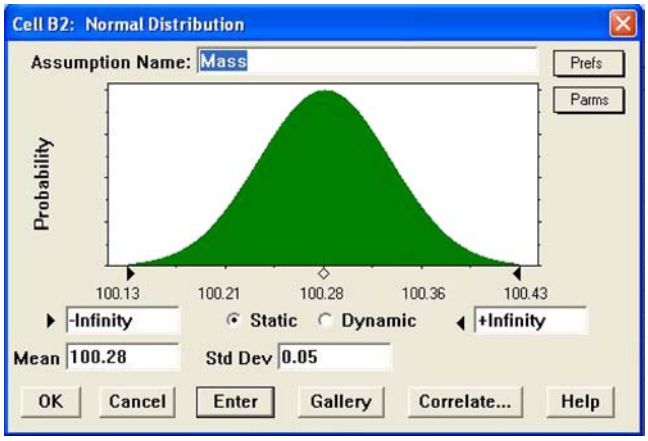


Fig. 20 Introduction of input data distributions in Crystal Ball

Uncertainty Pro

An excellent program very easy to handle, especially after the reading of the help, that is concrete and essential. Diagrammatic calculation boxes appear, enabling the data introduction by clicking inside the cells. Each input variable has associated one uncertainty cell which can be activated or deactivated, where the different possibilities for uncertainty calculation are considered. The program enables, from the Administrator access level, the building of the calculation diagram, leaving blank the values of input variables but with their uncertainties. Thus, authorized users when activating the diagram, only are aware of introducing the experimental data and obtain the corresponding report. The Administrator is the only person who has total access to modify the diagram. This fact makes the possibility of using

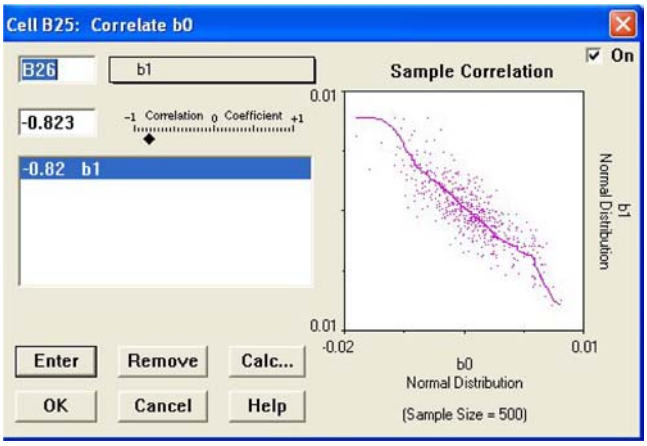


Fig. 21 Establishment of correlation between two input variables in Crystal Ball

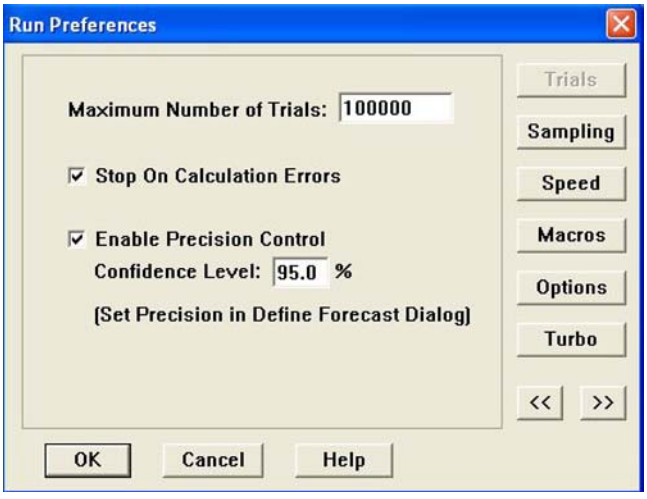


Fig. 22 Selection of simulation characteristics in Crystal Ball

the program in labs with different technicians, who actually do not need to know the full estimation of uncertainty measurement, but just introduce the experimental data. Besides, from the Administrator level, all performed jobs can be controlled because all movements performed in the user's accounts are recorded. This is a value added for labs involved in accreditation process or in good laboratory practices issues. The corresponding captures are presented in Figs. 9–12.

Decision Pro

This is a complex program to carry out a Monte-Carlo simulation. The help gives some basic foundations but not much else. The use of the program is somewhat awkward with complicated models. Another handicap is the lack of showing percentiles different from 5 and 95% for the output distribution. In Fig. 13, the data introduction by means of the decision tree is shown. The selection of the distribution features for input variables is illustrated in Fig. 14. The consideration of correlated variables is gathered in Fig. 15 and the output results are depicted in Fig. 16.

@Risk

This program is an Excel add-in that improves significantly the spreadsheet. Input data are introduced together with their distribution features, and the measurand output is estimated from the input values. Thus, this program can be of interest to those who use Excel spreadsheets. The videotutorial and the program help are good and suitable for getting started. The screen captures are shown in Figs. 17–19.

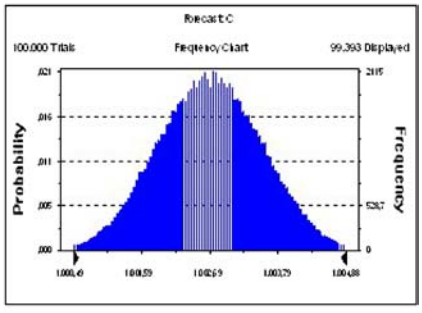
Fig. 23 Output report by Crystal Ball

Crystal Ball Report
Simulation started on 23/1/05 at 0:34:50
Simulation stopped on 23/1/05 at 0:37:07

Forecast: C **Cell: B9**

Summary:
Display Range is from 1.000,49 to 1.004,88
Entire Range is from 999,53 to 1.006,02
After 100.000 Trials, the Std. Error of the Mean is 0,00

Statistics:	Value
Trials	100000
Mean	1,002.71
Median	1,002.71
Mode	—
Standard Deviation	0.83
Variance	0.69
Skewness	0.01
Kurtosis	2.81
Coeff. of Variability	0.00
Range Minimum	999.53
Range Maximum	1,006.02
Range Width	6.48
Mean Std. Error	0.00



Crystal Ball

This is another Excel add-in. The introduction of input data and selection of distributions is very easy. The help explains in a superb way the simulation process. The "custom" distribution is a very good device, because it enables the introduction of both discrete and continuous records in a fully flexible way. The program can create a report with a lot of information within the Excel book and is lighter than @Risk. Important captures are shown in Figs. 20–23.

Conclusion

The commercial programs compared here can be used with success for the estimation of the uncertainty measurement. However, according to the feasibility, suitability and user-friendly features, the best programs are: Uncertainty Pro for classical GUM approach and Crystal Ball for Monte-Carlo simulations.

References

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