UNCERTAINTIES EVALUATION IN CHEMICAL ANALYSES USING ELECTRONIC SPREADSHEET. A USER-FRIENDLY APPROACH.

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Abstract

An electronic spreadsheet is used to facilitate the uncertainty evaluation in chemical analyses. A user-friendly and logical input of the entries is formatted driving the analyst during or to the data acquisition.

Keywords: uncertainty, chemical analysis, electronic spreadsheet

1. INTRODUCTION

Many are the contributions to the process uncertainty. Chemical analyses are usually a sequence of steps each one consisted of one or more operations. The more the operations the more the number of parameters that can be or must be considered in the uncertainty evaluation. A well known and controlled procedure is not a guaranty of a successful uncertainty evaluation even for a senior analyst. Although the mathematical operations are relatively simple in the uncertainty evaluation, the related statistics concepts and equations can bring the analyst to a "twilight zone". Certainly, training courses can help. Certainly, training courses are not the unique solution. Considering that the analytical procedure is not the problem, the analyst must, at least, be conscious of what he or she is calculating. As defined, the uncertainty represents the dispersion of the quantity values attributed to a measurand. This is what the calculations must show: dispersion.

Knowing that, the analyst must provide the inputs acquired during the process. The initial action is to list the procedure steps and all the parameters that take part in these steps and can influence theses parameters. An extensive list can fulfill all the contributions to the procedure. This is the first moment the analyst can get into trouble. The Ishikawa or fishbone diagram is very helpful to organize these parameters. But, if the analyst is intending to consider all these parameters, the calculation will consume a huge effort for a questionable increment in the result. As a first approach, a more complete list is desirable, but based on his or her experience the analyst will soon realize which parameters really are significant to the process. For a quality system requirements, laboratory compliance and conformity with ISO/IEC 17025[1], for instance, a more complete report is desirable in the first study. The evaluation of these influences will support the decision of what are those parameters that are really significant to the uncertainty and must be considered in the calculations.

In the uncertainty calculations one can not run the calculations using any set of acquired values. First of all, the data must be stable, in another words, the standard deviation must be tested and compared to a limiting value. This value can be established by the analyst, by the process or by the client. In processes sensitive to a data normal distribution, a test like Shapiro-Wilk [2] must be applied. In the most cases, the data are distributed in a normal distribution within the set of measurements.

In a chemical analysis the analyst will use balances, pipettes, volumetric glassware, standards materials, instrument to measure physical-chemical parameters, and so on. These items require a controlled environment, that is, humidity and temperature must be controlled; require calibration, that is, periodically any instrument, device, apparatus, that is used to perform a measurement must be compared and/or adjusted to a conventional true value. The certificates of the standards must report the uncertainty associated to the certified value. These are only a short list of common sources of uncertainty contributors.

The use of electronic spreadsheets really helps with all the calculations associated to whole process. A skilled analyst can use his or her knowledge and time in creating a spreadsheet that works. For a small number of processes, spreadsheets can be managed to run the calculations. As the calculations did not demand complex operations, the choice was to develop the spreadsheet in Microsoft Excel and to use VBA to run some works.

2. OBJECTIVE

A user-friendly approach based on the Microsoft Excel spreadsheet is proposed to evaluate the uncertainties of a chemical analysis. One of the aims of this approach is not to suggest a minimal set of parameters in each step, but to propose to the

analyst a pre-selected list of the most common and significant influences at each step. The analyst, in this way, will have an idea of what parameter is necessary to perform tests in order to obtain data.

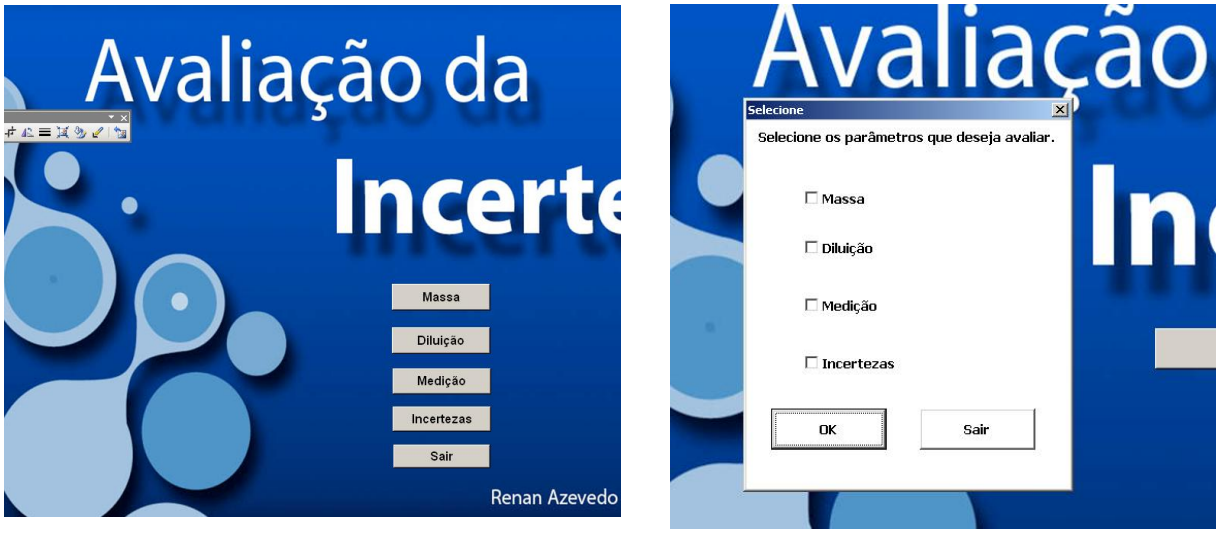
3. METHODS AND MATERIALS

Microsoft© Office Excel 2003 running in Microsoft© Windows XP Platform was used to develop the spreadsheets. Calculations were distributed in the worksheets as we consider the easiest way to understand and follow the spreadsheet sequence. Different background colors were used to identify entry data cell, result cell, reference or retrieving information cell. Comments to the cells were added showing equations and formulae, concepts and fundamentals, special comments to the cell value, reference source, directions to the next step, and so on. Whenever possible, the entire equations were written in a single cell and not divided in partial calculations. This can demands a lot of work writing long equations, but facilitates when an error has to be find by using the Excel formula evaluator. Visual Basic for Applications, VBA, was used to run some works. Bottoms were added to open panels or to run a calculation. Graphics were generated to a visual evaluation.

Most of the equations used in this work were withdrawn from the Eurachem/CITAC Guide [3]. Several others references were used to compose this work [2, 3, 4, 5, 6, 7]

4. RESULTS

Organizing the data entry in the major processes, the whole analytical procedure can be easier understood and the values can be acquired with minimum error or reworking. The initial worksheet of this spreadsheet shows a clear title and several bottoms to be selected on the choice of the analyst. In Figure 1, one can see the configuration of the first worksheet. As long as new features will be added, this configuration will change placing new bottoms or creating clusters of similar or sequential parameters.



a **b**

Figure 1: Partial view of the initial worksheet. Bottoms in the right side open specific worksheets that calculate the uncertainties in each step, a. A possible variation in this page is selecting the parameters in a panel, b.

In the worksheet identified as "Massa", Figure 2, the data about the mass, balance, outliers, normality and correlated parameters are evaluated. For a set of 7 mass replicates, the worksheet will show the average, standard deviation, variance residues and the uncertainty of this set of measurement. A graphic of these residues is displayed facilitating the evaluation of an eventual bias during the process. To compose the balance control, chart control using both mass measurement and standard deviations of the data will be added. This will be done by creating a new worksheet or panel fed by exporting or linking these data. In evaluating the uncertainty, a control chart based on standard deviation will show if the process is stable or is within the limits or some agent is acting on the balance. Sometimes, just reading the standard deviation chart control, one can find out that the process is about to get out control.

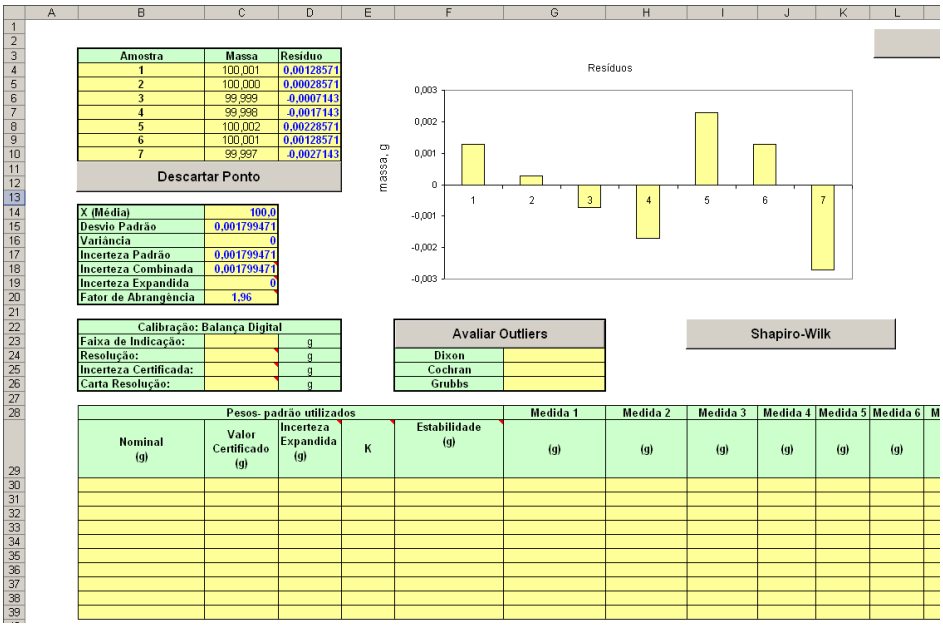
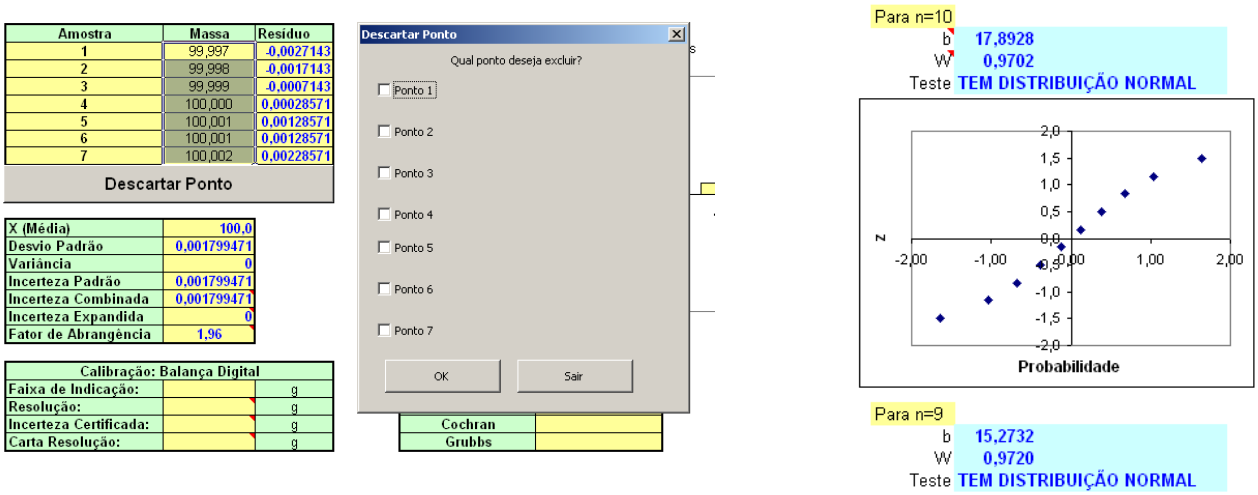


Fig. 2: A worksheet with evaluation of mass data. Outliers and normality tests are included.

Tests for outliers are performed using Dixon, Cochran and Grubbs approach. In the Outliers box, only the information of detected or not detected is displayed. The value considered as outlier is showed in another panel accessed by the "Avaliar Outliers" bottom. If there is a outlier in the set, this one can be took out by clicking the "Descartar Ponto" bottom, Fig. 3a, and selecting the outlier.

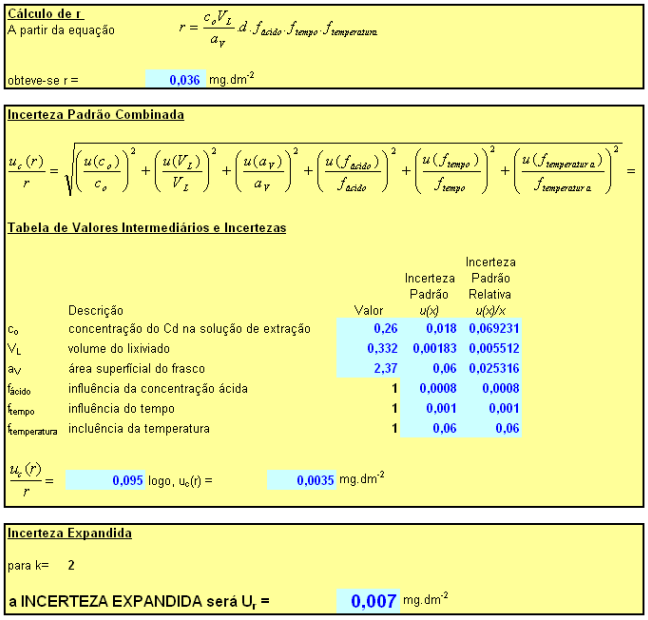
The data normality is evaluated clicking the bottom "Shapiro-Wilk", Fig. 3b. A new worksheet is opened showing a graphic and a message informing if the data are normal distributed or non-normal distributed.



(a) **(b)**

Fig 3.: Excerpt showing the panel where the outlier can be selected, a, and the Shapiro-Wilk test for a set of values, b.

An example of combining the uncertainties is showed in Fig. 4 and Fig. 5. For a given process, represented by the equation *r*, Fig. 4, the standard and relative uncertainties are calculated for each parameter. The combined and the expanded are calculated in the following. A continuous improvement expected to this page is to show the Ishikawa diagram next to these results, with the uncertainty values of each parameter (numeric legend or bars), in order to provide the analyst with a visual tool of the process.



Cálculo de r

A partir da equação $r = \frac{c_o V_L}{a_V} d \cdot f_{ácido} \cdot f_{tempo} \cdot f_{temperatura}$

obteve-se r = 0,036 mg.dm^{-2}

Incerteza Padrão Combinada

$$\frac{u_c(r)}{r} = \sqrt{\left(\frac{u(c_o)}{c_o}\right)^2 + \left(\frac{u(V_L)}{V_L}\right)^2 + \left(\frac{u(a_V)}{a_V}\right)^2 + \left(\frac{u(f_{ácido})}{f_{ácido}}\right)^2 + \left(\frac{u(f_{tempo})}{f_{tempo}}\right)^2 + \left(\frac{u(f_{temperatura})}{f_{temperatura}}\right)^2} =$$

Tabela de Valores Intermediários e Incertezas

	Descrição	Valor	Incerteza Padrão u(x)	Incerteza Padrão Relativa u(x)/x
c_o	concentração do Cd na solução de extração	0,26	0,018	0,069231
V_L	volume do lixiviado	0,332	0,00183	0,005512
a_V	área superficial do frasco	2,37	0,06	0,025316
$f_{ácido}$	influência da concentração ácida	1	0,0008	0,0008
f_{tempo}	influência do tempo	1	0,001	0,001
$f_{temperatura}$	incluência da temperatura	1	0,06	0,06

$\frac{u_c(r)}{r}$ = 0,095 logo, $u_c(r)$ = 0,0035 mg.dm^{-2}

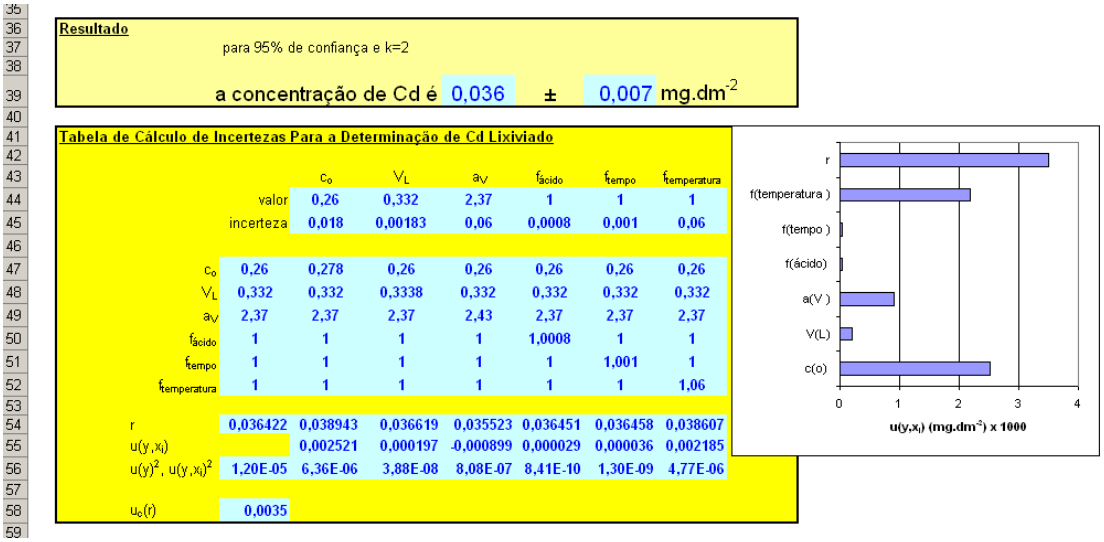
Incerteza Expandida

para k= 2

a INCERTEZA EXPANDIDA será U_r = 0,007 mg.dm^{-2}

Fig. 4: Excerpt showing the standard, the relative, the combined and the expanded uncertainties.

In the sequence, just below in the worksheet, the uncertainties are showed graphically. As one can see, some parameters uncertainties are negligible in the whole process. The analyst can, after this study, select only those parameters really significant and save time without loosing information. As a continuous improvement, a process indicator tool in this step will be considered in order to help the analyst to recalculate the whole process uncertainty without extracting, separating or taking out values in the previous worksheets. A bottom will be added opening a panel where the negligible parameters could be selected and removed from the final calculations.



Resultado

para 95% de confiança e k=2

a concentração de Cd é 0,036 ± 0,007 mg.dm^{-2}

Tabela de Cálculo de Incertezas Para a Determinação de Cd Lixiviado

	c_o	V_L	a_V	$f_{ácido}$	f_{tempo}	$f_{temperatura}$
valor	0,26	0,332	2,37	1	1	1
incerteza	0,018	0,00183	0,06	0,0008	0,001	0,06
c_o	0,26	0,278	0,26	0,26	0,26	0,26	0,26
V_L	0,332	0,332	0,3338	0,332	0,332	0,332	0,332
a_V	2,37	2,37	2,37	2,43	2,37	2,37	2,37
$f_{ácido}$	1	1	1	1	1,0008	1	1
f_{tempo}	1	1	1	1	1	1,001	1
$f_{temperatura}$	1	1	1	1	1	1	1,06
r	0,036422	0,038943	0,036619	0,035523	0,036451	0,036458	0,038607
u(y,x$_i$)		0,002521	0,000197	-0,000899	0,000029	0,000036	0,002185
u(y)^2, u(y,x$_i$)^2	1,20E-05	6,36E-06	3,88E-08	8,08E-07	8,41E-10	1,30E-09	4,77E-06
u_c(r)	0,0035						

Fig. 5: In this excerpt, the contribution of each uncertainty is showed graphically.

This project is not intended to be exhaustive and, in the present situation, it is still incomplete.

One of the next features to be added is to create and to show the Ishikawa diagram with labels in the branches after selecting the entry parameters. This will be very helpful to evaluate visually if the parameters were selected accordingly to the analysis. Another tool already considered to be added is the possibility to simulate variations in the entry data and see in

the final result the effects of these conditions. Of course, it can be done right now just changing the entry data. But in a user-friendly way, the analyst can explore other possibilities without losing the control within the data. The visual design will also be improved trying to become more clearly the data entry and the result visualization and interpretation.

Uncertainty evaluation using the Monte Carlo Method is also being considered as the personal computers are already powerful enough to run large data collection. The method does not depend on the linearity of the mathematical models or on the normal distribution of the data. To the analyst, it means that the normality test is no more necessary. In the other hand, the mathematical model must be as closest as to the actual behavior.

5. CONCLUSIONS

A user-friendly approach is very helpful to calculate the uncertainties using the Microsoft Excel spreadsheet.

All the raw calculations derived from the equations do not need to be showed and can be hidden. If needed, the general formula can be showed as an added comment. As a result, the worksheets present clear workspaces and only the necessary information are displayed or asked. The hidden formulae are protected from accidental changes.

Following the panels or the worksheets, the analyst can plan and organize the time needed to run the study.

As Microsoft Excel is easy to edit, worksheets can be added and the partial results can be easily retrieved to further calculations. This full editing capability can be used by the analyst to learn more or to customize the calculations as necessary.

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