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VALIDATION AND ASSESSMENT OF UNCERTAINTY OF CHEMICAL TESTS AS A TOOL FOR THE RELIABILITY ANALYSIS OF WASTEWATER IPEN

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ABSTRACT

The validation of analytical methods has become an indispensable tool for the analysis in chemical laboratories, including being required for such accreditation. However, even if a laboratory using validated methods of analysis there is the possibility that these methods generate results discrepant with reality by making necessary the addition of a quantitative attribute (a value) which indicates the degree of certainty the extent or the analytical method used. This measure assigned to the result of measurement is called measurement uncertainty. We estimate this uncertainty with a level of confidence both direction, an analytical result has limited significance if not carried out proper assessment of its uncertainty. One of the activities of this work was to elaborate a program to help the validation and evaluation of uncertainty in chemical analysis. The program was developed with Visual Basic programming language and method of evaluation of uncertainty introduced the following concepts based on the GUM (Guide to the Expression of Uncertainty in Measurement). This evaluation program uncertainty measurement will be applied to chemical analysis in support of the characterization of the Nuclear Fuel Cycle developed by IPEN and the study of organic substances in wastewater associated with professional activities of the Institute. In the first case, primarily for the determination of total uranium and the second case for substances that were generated by human activities and that are contained in resolution 357/2005. As strategy for development of this work was considered the PDCA cycle to improve the efficiency of each step and minimize errors while performing the experimental part. The program should be validated to meet requirements of standards such as, for example, the standard ISO / IEC 17025. The application, it is projected to use in other analytical procedures of both the Nuclear Fuel Cycle and in the control program and chemical waste management of IPEN.

1. INTRODUCTION

The validation of analytical methods has become an essential tool for the analyses in chemical laboratories, including those required for such accreditation. This validation is intended to ensure the quality needed for the analytical result, obtaining reliability in qualitative and quantitative analysis, establish confidence and credibility to the analytical laboratory and the method chosen or developed.

This whole process is evaluated using statistical tools to check and ensure that result is as close as possible to the true or conventional value. Not always performed in the validation studies, the uncertainty estimation is an important information attributed to the chemical analysis result. This paper focuses on this stage of validation.
The data generated in the validation study represent the overall performance of a method and points out the interference of individual factors on the total uncertainty, making these results applicable to the evaluation of uncertainty measurement.

We can estimate this uncertainty with a certain level of confidence using experimental data obtained from the requirements established by the process or by the client. In this sense, an analytical result has limited significance if not carried out with proper assessment of its uncertainty.

In nuclear reactors, the control of chemical analyses supported by a quality system provides greater quality throughout the process life cycle. Not necessarily, but accredited analyses tend to play a more important role even in this moment that nuclear energy is observed from all sides.

As the environmental concern is worldwide, the software developed is also applied to the analysis of effluents generated at IPEN. Organ chlorinated compounds such as chloroform, dichloroetene, phenol, tetrachloridecarbon and trichloroethylene are considered compounds harmful to health in accordance with the resolution 357/2005 and 397/2008 CONAMA in Brazil and are being analyzed and the measurement uncertainties estimated using this software. As a part of the whole process, data can show some lack in details as uncertainty sources of different input quantity are obtained or calculated depending on the information availability. These many steps can allow the introduction of errors or failures that may impair or distort the quality of the result (uncertainty).

Therefore, the aim of this study was to develop software able to promote the method validation and evaluate the uncertainty in chemical analyses running in an organized manner in order to improve the knowledge of the analyst about the process, minimizing the dispersion of results due to possible errors or deviations in these analyses.

2. STUDY OF UNCERTAINTY IN MEASUREMENT

Initially, it is necessary to know the process or analytical procedure. Thus, the analytical skills to direct all actions that include: a list of all operations (including the input quantities) carried out in the analytical procedure, the organization of such operations in the form of a flowchart and a mathematical equation that defines the measuring a function of the input, the ratio of all sources of uncertainty for each input quantity. Depending on the measuring, you can define from the outset the method of uncertainty estimation to be used.

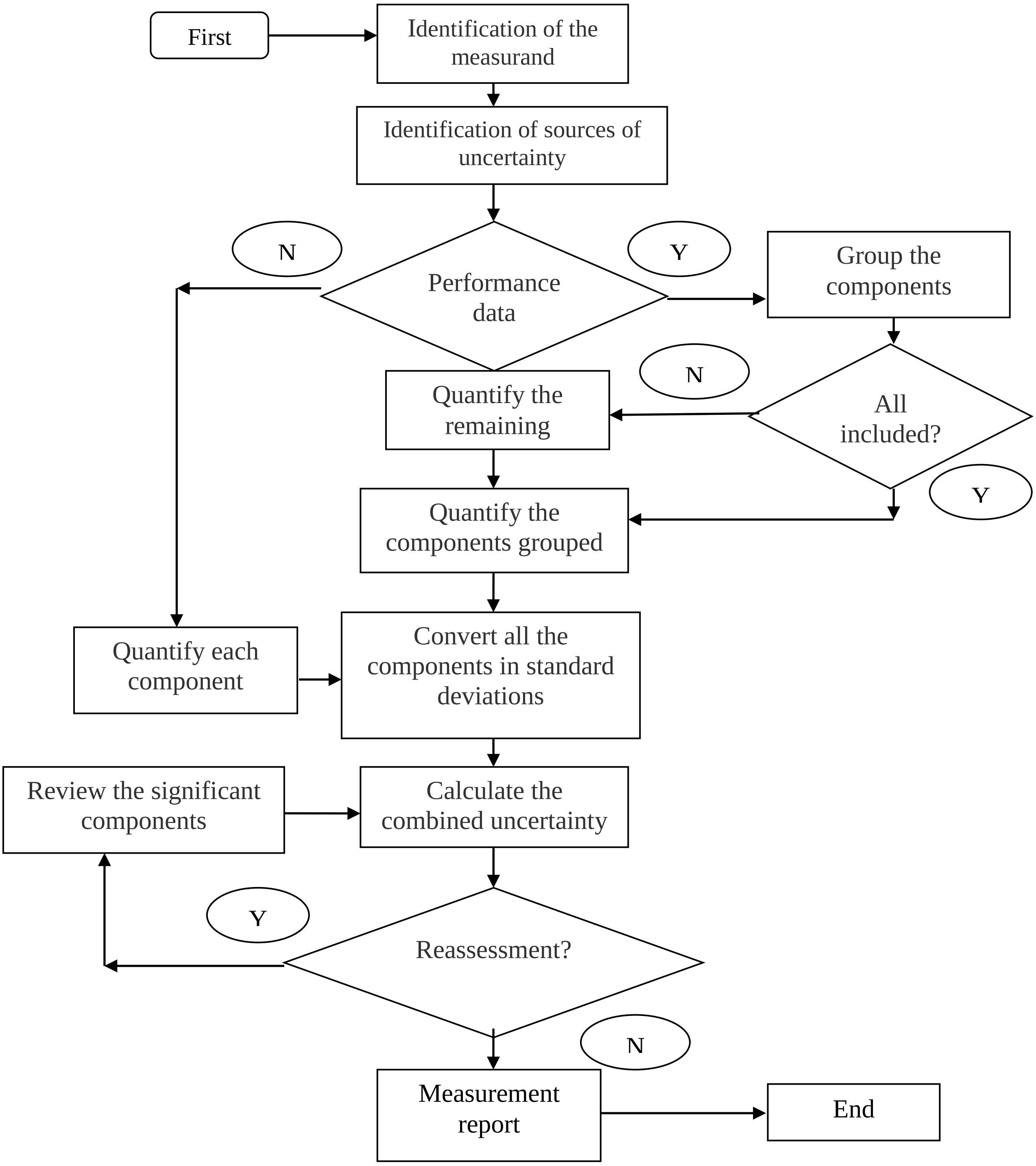

Figure 1. Flowchart representing the process of obtaining the value of uncertainty

If there are sources of uncertainty not accounted for properly, should be sought additional information or documentation in the literature as awards, certificates and specifications. Uncertainties can be classified into two types: Type A and Type B. If the uncertainty obtained for a given parameter takes into account the statistical distribution of a series of measurements, this uncertainty is called the uncertainty of type A. This type of evaluation is characterized by experimental standard deviation and is typically used to obtain a value for the repeatability of a measurement process.

If the uncertainty for a given parameter takes into account the probability distribution assumed, based on experience or other information such as a certificate, this uncertainty is called the uncertainty of type B. This type of contribution is assessed through a scientific judgment based on all possible information about the variability of the input, in other words, all factors that can influence a measurement.

3. THE LOGIC OF THE CALCULATIONS OF THE SOFTWARE

The method used to calculate the uncertainty in the evaluation software is the uncertainty from the measurements of individual components of uncertainty that considers both type A and type B uncertainties.

The procedure used in the combination of individual components is to evaluate the standard uncertainties associated with individual parameters and combine them according to the law of propagation of uncertainty.

Initially, all the contributions of the uncertainties should be expressed as standard uncertainty for each component. The standard uncertainty is quantified in terms of standard deviation of the measured values. The standard deviation is obtained using the following equation:

$$. \ s = \sqrt{\frac{\sum (xi - x)^2}{N - 1}} \tag{1}$$

The result as individual standard uncertainty is used to calculate the combined standard uncertainty, according to the link below:

$$. \ u_c(y(x_1, x_2, ...)) = \sqrt{\sum_{i=1,n} c_i^2 u(x_i)^2} = \sqrt{\sum_{i=1,n} u(y, x_i)^2} \tag{2}$$

Each contribution of the variable u (y, x) is the square of the uncertainty expressed as standard deviation multiplied by the square of the coefficient of sensitivity.

The combined uncertainty value must be multiplied by a coverage factor generating the expanded uncertainty appropriate for a range of confidence.

The coverage factor, k, is obtained from the effective degrees of freedom and is directly related to sample size. This factor is obtained by the Welch-Satterthwaite equation, shown below:

$$\nu_{eff} = \frac{[u_c(y)]^4}{\sum_{i=1}^{n} \frac{[u_i(y)]^4}{\nu_i}} \quad (3)$$

After these steps, the uncertainty value calculated by the software is exported as recommended by the ISO GUM guide, with all operations of the process of evaluating the uncertainty of the analytical method, thus allowing to identify which probability distributions were assumed for each component of, which uncertainty the effective number of degrees, what is the coverage factor used and all other parameters.

The conduction of the uncertainty estimation can be carried out by selecting the following methods: Classic, Relative, Kragten and Monte Carlo.

This option window is enabled to user only after all input quantities are calculated. User can choose the appropriate method to estimate the uncertainty. Help texts is provided to support the selected choice. This procedure is shown in Figure 5.

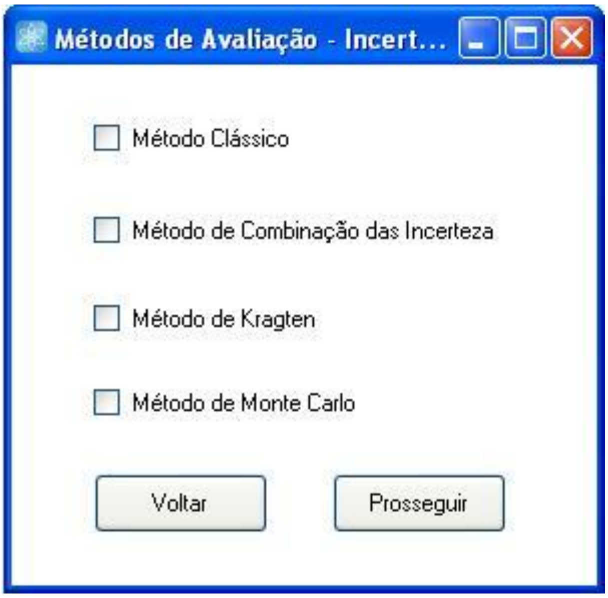

Figure 5. Area selection method to be used for the calculation of uncertainty.

With a different approach, the Monte Carlo method for uncertainty estimation is based on randomically generation of values for each uncertainty source for all input quantities within a known or probable range. This method is now under development in Visual Basic programming language. As can be seen in the Fig. XX, the Monte Carlo method is just ready to run in a Microsoft Excel spreadsheet and this design will be used in the configuration using the Visual Basic language.

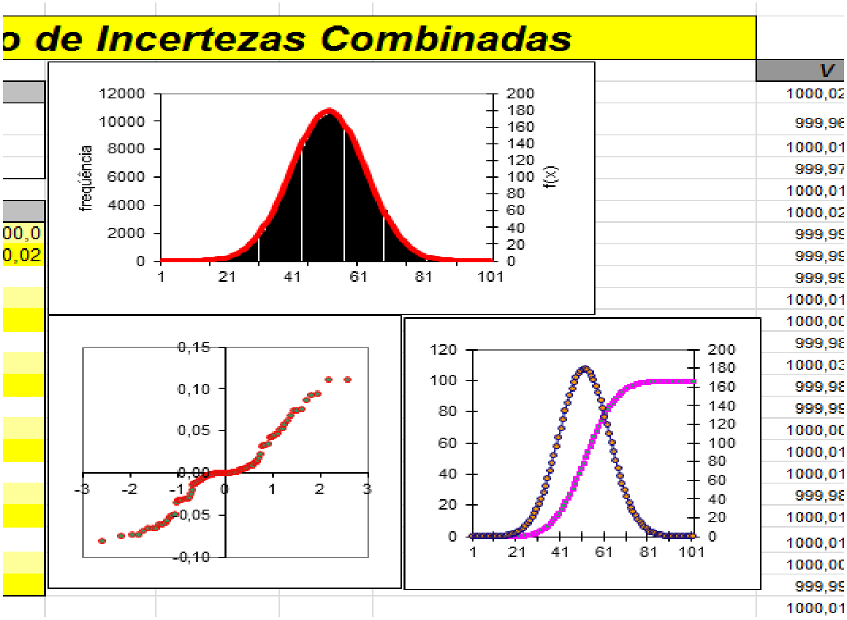

Figure 6. An example of output calculation of uncertainty measurement by Monte Carlo method using Microsoft Office Excel.

Regarding the common strategy for evaluation of uncertainty compared with the strategy used by the software, the software offers a better organization of the data and the results are obtained more quickly and accurately. The user can simultaneously place where the declaration of the input data to understand the relevance of each stage of evaluation of uncertainty in the outcome.

As an example, one can cite the preparation of a solution of sodium hydroxide with a concentration of 40 gL-1.

In this process, one should take into account the uncertainty declared by the manufacturer in the use of volumetric flask, the uncertainty of the resolution scale and the standard deviation related to the weights carried by the user.

If getting the result of uncertainty was performed by the software, just declare the variables in the tabs "Massa" and "Volume" obtaining the standard uncertainty for both steps. The value of the expanded uncertainty would have to be calculated separately, because the software only generates values for this result to complete process of uncertainty evaluation for chemical analysis (which extends from the stage of preparation of standard solutions, the evaluation of the calibration curve until the temperature of the laboratory).

But if the uncertainty evaluation was conducted through the joint strategy, there would need to calculate the uncertainty type A repeats of the weights, the uncertainty type B for the resolution of the scale, the standard uncertainty for this step and the uncertainty related to the type B flask used in the preparation of the solution and the expanded uncertainty.

In this way, the strategy used by the software becomes faster and also decrease the chances of errors, because the organization of the calculations can confuse the analyst.
However, for isolated steps, such as assessing the value of uncertainty for processes that encompass only the volume and mass as in this case, the software does not generate the value of expanded uncertainty, and thus it should be calculated using the normal strategy.

4. PROGRAMMING SOFTWARE

The program was written using Microsoft Visual Basic (Microsoft Visual Basic 2008 Express Edition). The idea was to develop not only an application to facilitate the calculation of uncertainty, but a simple interface allowing users exploring through the panels and definitions.

All parameters evaluated in obtaining the value of uncertainty are defined and explained according to the Eurachem guide topics, so users can know how the calculations are being made and follow the process of obtaining the value of uncertainty. The following example represents the process of obtaining the value of the mass measurement combined uncertainty. The parameter to be evaluated can be selected among others and a new panel is opened to input data.

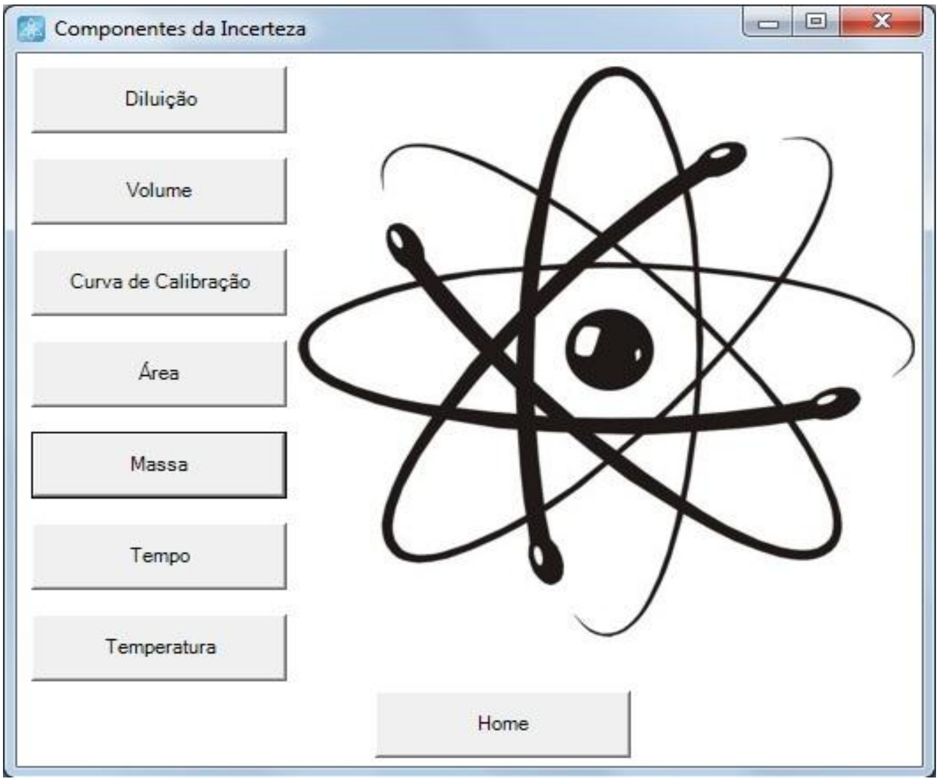

Figure 2. Selection area of the parameter to be evaluated.

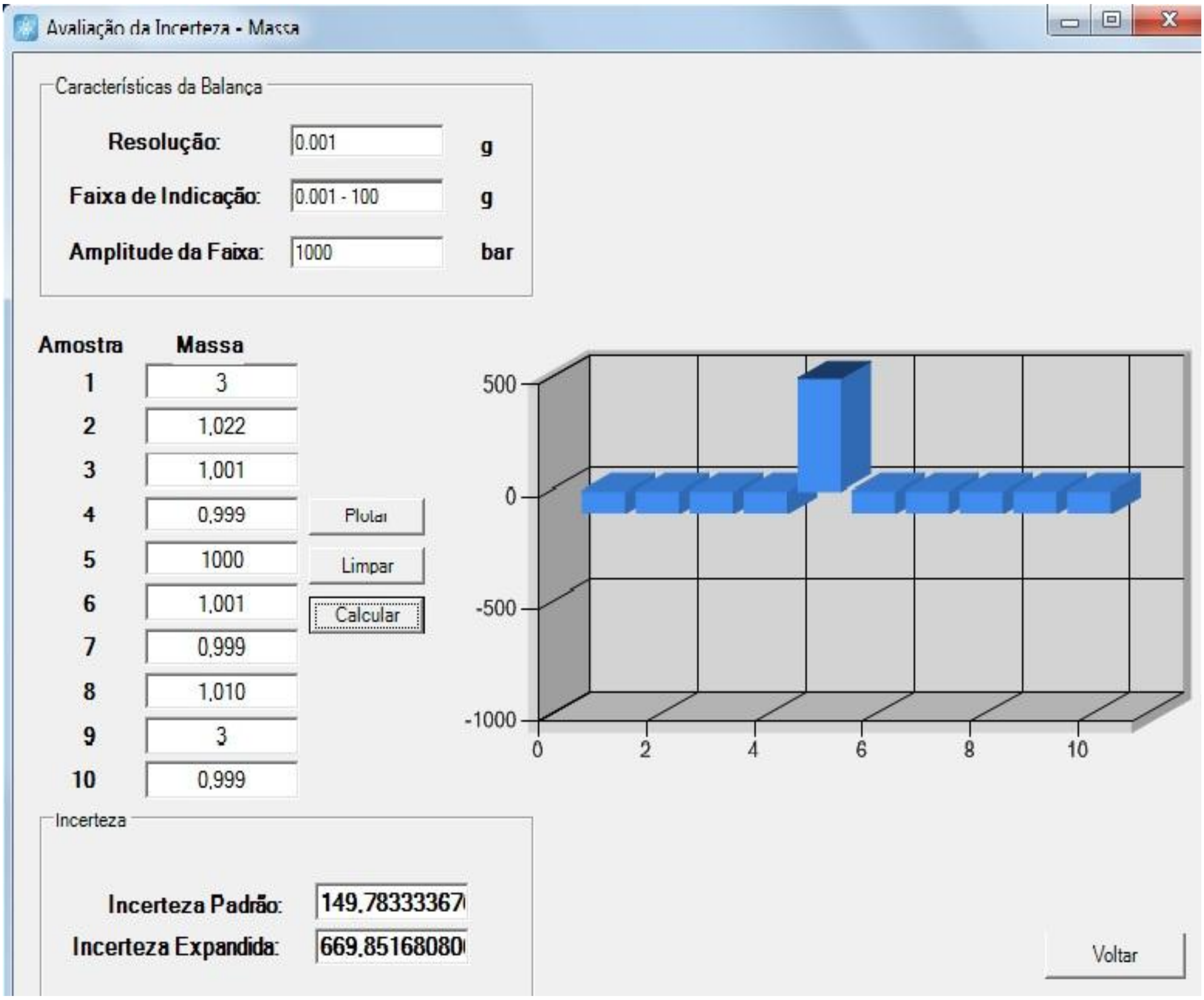

Figure 3. Area where the variables are declared for the calculation of the uncertainty in the mass measurement.

The uncertainty calculation performed by the software includes simple math, and was carried out as shown below:

```
Private Sub Button3_Click(ByVal sender As System.Object, ByVal e As
System.EventArgs) Handles Button3.Clic

    If TextBox1.Text = "" Or txtMassa1.Text = "" Or txtMassa2.Text = "" Or
txtMassa3.Text = "" Or txtMassa4.Text = "" Or txtMassa5.Text = "" Or txtMassa6.Text
= "" Or txtMassa7.Text = "" Or txtMassa8.Text = "" Or txtMassa9.Text = "" Or
txtMassa10.Text = "" Then
        MsgBox("Dados Insuficientes.")
    Else
        Dim num1, num2, num3, num4, num5, num6, num7, num8, num9, num10,
num11, Media, Desvpad, Urep, Res, Upad, Ucomb, Uexp As Decimal

        num1 = txtMassa1.Text
        num2 = txtMassa2.Text
        num3 = txtMassa3.Text
        num4 = txtMassa4.Text
        num5 = txtMassa5.Text
        num6 = txtMassa6.Text
        num7 = txtMassa7.Text
        num8 = txtMassa8.Text
        num9 = txtMassa9.Text
        num10 = txtMassa10.Text
        num11 = TextBox1.Text

        Media = (num1 + num2 + num3 + num4 + num5 + num6 + num7 + num8 +
num9 + num10) / 10

        Desvpad = Math.Sqrt(((num1 - Media) ^ 2) + ((num2 - Media) ^ 2) + ((num3 -
Media) ^ 2) + ((num4 - Media) ^ 2) + ((num5 - Media) ^ 2) + ((num6 - Media) ^ 2) +
((num7 - Media) ^ 2) + ((num8 - Media) ^ 2) + ((num9 - Media) ^ 2) + ((num10 -
Media) ^ 2))

        Urep = Desvpad / Math.Sqrt(10)

        Res = (num11 / 2) / Math.Sqrt(3)

        Upad = Urep / 2

        Ucomb = Math.Sqrt((Urep ^ 2) + (Upad ^ 2) + (Res ^ 2))

        Uexp = Ucomb * 2

        TextBox4.Text = Upad
        TextBox5.Text = Uexp

    End If
End Sub
```

Figure 4. Programming the calculation of the uncertainty in the dilution performed in software.

5. EXPORTING RESULTS

After performing the analysis of registered data, is generates a text file containing all the parameters of the uncertainty measurement carried out in report form. All analysis performed by the software generates a file of this type, making it possible to access the information later, printing or format the report.

The report from analysis of data generated by the software contains the description of the method used to calculate the uncertainty, the amounts and sources of all corrections and constants used in the calculation analysis of uncertainty and a list of all the components of uncertainty. In addition, the relationship is provided between the output and input values and the number of degrees of freedom for the standard uncertainty of each input value.

The value of the expanded uncertainty is stated in the form (x ± U) (units) where x represents the amount issued and U represents the value of the expanded uncertainty using a coverage factor equal k. The value of k used to calculate the expanded uncertainty is also reported. However the process of issuing a report by the software is still under development since the intention is to add more variables to make the process more concise evaluation of uncertainty, export more parameters for data analysis such as graphs and charts for routine the report is more complete and the report can be filed in Portable Document Format (PDF). The page editor of the report is shown in figure 5.

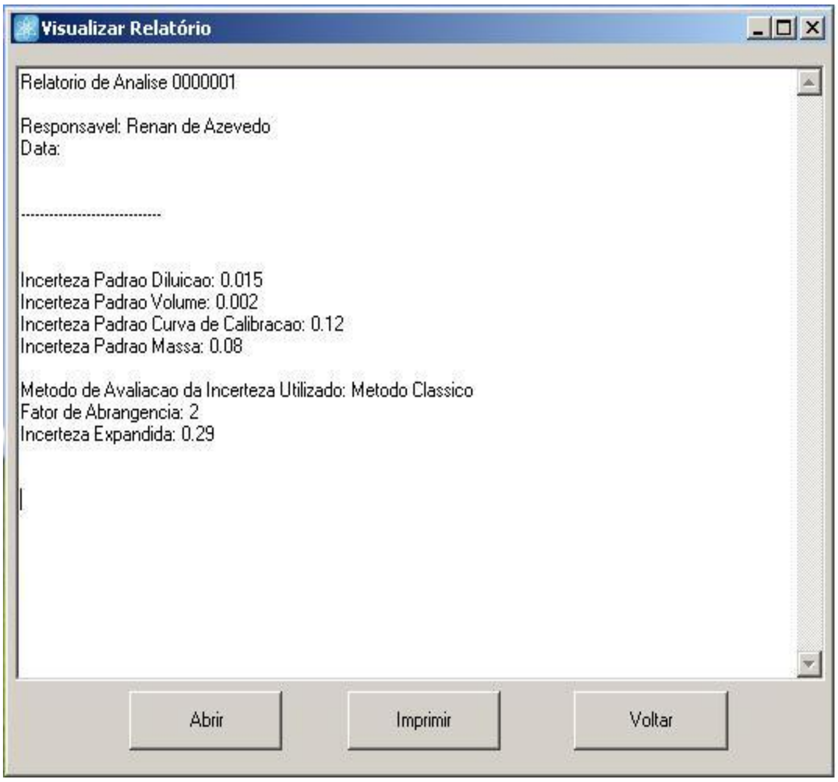

Figure 5. Page editor of the report.

6. CONCLUSION

The software described in this paper organizes the data obtained in chemical analysis and performs the uncertainty evaluation for such processes. Formerly, it was applied to environmental analyses and now is in a development step to the nuclear fuel analyses.

With a friendly interface, one can follow the process of measurement uncertainty estimation and understand the influence of an individual factor on a specific input quantity or to the whole process.

All parameters were set according to the VIM, which tells the user the relevance of each step and how the calculation is performed.

If needed, the software can be adapted or modules added to generate estimates of uncertainty in other tests such as in ecotoxicology, biology and biomedical analysis, for example.

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