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UNCERTAINTIES SOURCES EVALUATION ASSOCIATED TO SULFUR AND FLASH POINT IN DIESEL FUEL

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Abstract: The international trade, the environmental protection and the science, today, cannot be able to exist without reliable measurements. Nowadays, any results of measurement of a physical or chemical quantity should be accompanied for any quantitative indication of the quality of this data, in order to be able to evaluate its reliability. Thus, an easy concept known and with wide acceptance that could characterize the quality of the result of a measurement is expressed by its uncertainty. In this work, we will present the application of the ISO GUM 95 for estimating uncertainty in the following tests: sulfur and flash point in diesel fuel. This research includes the development of a software based on Delphi version 6.0 to calculate the possible sources of uncertainty associated to the measurement used in both process and an estimation of their value, either by statistical methods (Type A) or by other means (Type B). Later on the individual components are combined to calculate the standard and expanded uncertainty for the whole process. The program developed aimed reducing the time spent in figuring out the main sources of uncertainty, moreover, facilitating the obtainment of the uncertainty result. To visualize the most relevant factor in the uncertainty measurement, the program provides a graphic showing the uncertainty contributions and enables the calculation of final uncertainty combined by the relative method, based on Eurachem/CITAC Guide, allowing the graphic comparison among the different methods in calculating uncertainty in measurement.

Key words: metrology, measurement uncertainty, diesel fuel

1. INTRODUCTION

With the advent of globalization and the consequent opening of the Brazilian economy to foreign markets, it is vitally important that Brazilian industries, laboratories, research centers etc, make haste to demonstrate the same levels of quality as those that they declare for their products and services, thereby assuring their place within the context of national and international competition [1].

Metrology, the science of measurement, plays a key role in society today. International trade, environmental protection and science cannot exist without reliable measurements. Nowadays, the result of any measurement of a physical or chemical quantity must be accompanied by a quantitative indication of the quality of this data for its reliability to be assessed. One simple, well-known, widely accepted concept that can characterize the quality of the result of a measurement is its uncertainty [2].

The losses that occur because of errors, production defects, and time lost in repeating work, excess waste and other types of wastage have risen to very high levels as a proportion of the Gross Domestic Product (GDP). Without doubt, metrology is central to much of this waste, for reasons such as i) the large number of instruments existing in Brazilian industries and laboratories that are too precise for the specific needs of a process, and ii) measurement errors in the sale of products.

Credibility of analytical data has never caught the public's eye more than today. The key principle for quality and reliability of results is comparability between laboratories and on a wider, international basis. In order to be comparable, analytical results must be reported with a statement of measurement uncertainty and they must be traceable to common primary references [3].

Liquid hydrocarbon fuels like diesel will remain the key transportation fuel for many years to come. Sulfur will be lowered worldwide still this decade. Next to sulfur there will be other properties that need to be improved. For diesel among others a new specification for aromatics is considered, but this item will not be discussed in this work. In order to guarantee security conditions, another property must be considered. Flash point is the lowest temperature at which a liquid can form an ignitable mixture in air near the surface of the liquid. The lower the flash point, the easier it is to ignite the material. Flash points are determined experimentally by heating the liquid in a container and then introducing a small flame just above the liquid surface. The temperature at which there is a flash/ignition is recorded as the flash point. Two general methods are called closed-cup and open-cup. The closed-cup method prevents vapors from escaping and therefore usually results in a flash point that is a few degrees lower than in an open cup. Because the two methods give different results, one must always list the testing method when listing the flash point.

The aim of this work is to develop a software based on Delphi version 6.0 to calculate the possible sources of uncertainty associated to the measurement used in both process: sulfur (according to ASTM D 4294) and flash point (according to ASTM D 56 and D 93) in diesel fuel samples and an estimation of the combined standard uncertainty measurement.

2. METHODOLOGY

To develop this work, the fundamentals of the International Organization for Standardization's Guide to the Expression of Uncertainty in Measurement, Geneva, 1993, revised and reprinted in 1995 – ISO GUM [4], were applied. This document provides an organized method for estimating uncertainty in measurements, without which no results could be compared. The ISO GUM is also established as a powerful tool for defining all the instrumentation in a given process.

In this work, we will present the application of the ISO GUM for estimating uncertainty in the following tests: i) sulfur in diesel fuel and ii) flash point in diesel fuel.

This research includes the development of a software based on Delphi version 6.0 to calculate the potential sources of uncertainty associated to the measurements used in both processes and a estimate of their value, either by statistical methods (Type A) or by other means (Type B). Later, the individual components are combined to calculate the standard and expanded uncertainty for the whole process. The software developed aims to reduce the time spent identifying the main sources of uncertainty, also facilitating the obtainment of the uncertainty results associated to the sulfur and flash point analysis of diesel fuel. To visualize the most relevant factors in the uncertainty measurement, the program provides a graphic showing the uncertainty factors involved in the operators, samples and equipments used. It also enables the calculation of final uncertainty combined by classic, simulated and relative methods, based on the Eurachem/CITAC Guide [5], allowing for a graphic comparison of the different methods for calculating uncertainty in measurements.

In the statistical analyses and in calculating the final expanded uncertainty, a pool of data of different samples was used, and all the tests were done at LABCOM in order to optimize the utilization of the program developed and identify which parameters are relevant to the measurement processes in question.

All experiments always include at least the repeatability of the measurements and this value was used to evaluate the overall experiment and to use the values from the method validation to quantify its size, leading to the revised cause and effect diagram [6].

3. RESULTS AND DISCUSSION

Dispersion of repeated measurements can be used as a parameter for making evaluations and decisions as to the repeatability and reproducibility of the measurement methods of operators, instruments, etc. In this study, an one-way ANOVA (Analyses of Variance) was used to determine the homogeneity between the results obtained by three operators including sulfur and flash point analyses in diesel fuel, in different days. Table 1 shows the principal matrix of observations of an one-way ANOVA.

Table 1. One-way ANOVA design

Factor	Data		Total
1	$Y_{11}Y_{12}Y_{13}$	Y_{1n}	$Y_{1.}$
2	$Y_{21}Y_{22}Y_{23}$	Y_{2n}	$Y_{2.}$
.			
.			
.			
a	$Y_{a1}Y_{a2}Y_{a3}$	Y_{an}	$Y_{a.}$
Total			Y..

Table 2 shows the results obtained from the analysis of variance, where it is possible to compare the F value (F0) to critical F value. In case that F value is superior to F critical value (95% of significance) it is possible to considerer the heterogeneity of variance of the operators involved on measurement process.

Table 2. One-way ANOVA

	df	SS	MS	F_0
Factor (operator)	a-1	SSF	QMF	QMF/QME
Error	N-a	SSE	QME	
Total	N-1	SST		

*df: degree of freedom

SS: sum of squares

MS: mean of squares

Where:

$$SST = \sum_i \sum_j \left(Y_{ij} - \overline{Y}..\right)^2 = \sum_i \sum_j Y_{ij}^2 - Y_{..}^2 / N \quad (1)$$

$$SSF = n\Sigma\left(\overline{Y_i}. - \overline{Y}..\right)^2 = \left(1/n\right)\sum Y_{i.}^2 - Y_{..}^2 / N \quad (2)$$

$$SSE = SST - SSF \quad (3)$$

It can be seen that the software developed allows the input of data on the sulfur measurement, the ambient temperature, calibration curve data, including information contained on the calibration certificates of the measurement instrument and the certified reference materials used in the tests [7].

The relevant uncertainty sources in sulfur measurements are shown in the cause and effect diagram below (Figure 1).

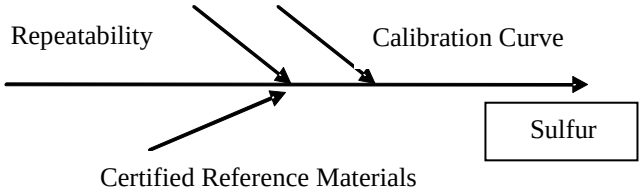

Figure 1. Cause and Effect Diagram

In this step the size of each identified potential source of uncertainty is either directly measured, estimated using previous experimental results or derived from theoretical analysis. Results are shown in Figure 2.

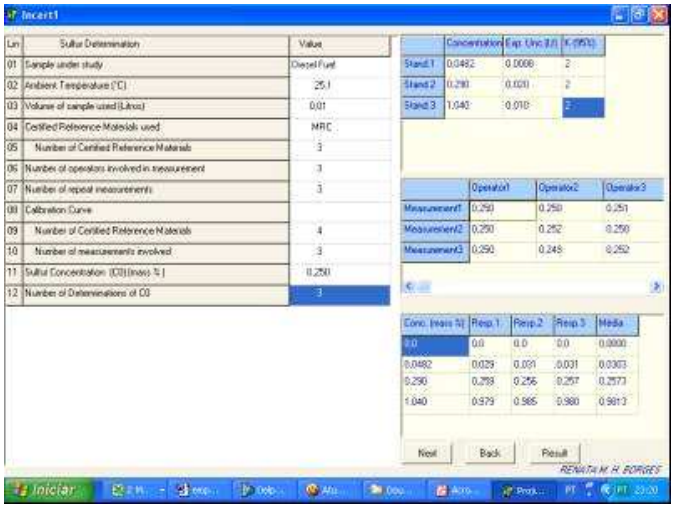

Fig. 2. Table containing initial sulfur measurements and analysis of the variance homogeneity

The calibration standards were measured and the line equation $A_j = C_i \cdot B_1 + B_o$ represent the analytical curve, where A_j j^{th} is the measurement of the degree of sulfur content from the j^{th} calibration standard, C_i is the concentration of i^{th} calibration standard and B_1 is the angular coefficient and B_0 is the intersection point with Y axis.

The standard uncertainty in relation to the concentration and the residual standard deviation (s) were calculated by the expressions below:

$$u_{C_0} = \frac{s}{B_1} \times \sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(C_0 - C)^2}{s_{xx}}} \quad (4)$$

$$s = \sqrt{\frac{\sum_{j=1}^{n} \left[A_j - (B_0 + B_1 \times C_j\right]^2}{n-2}} \quad (5)$$

$$s_{xx} = \sum_{j=1}^{n} (C_0 - C)^2 \quad (6)$$

where p is the number of the measurements to determine, C_0 n is the number of measurements for the calibration, C is the average value of the different calibration standards, i is the index for the number of calibration standards and j is the index for the number of measurements to obtain the analytical curve [5].

The combined standard uncertainty is done based on the errors propagation law, by 'root sum squares' of the individual uncertainties. Estimation of combined standard uncertainty was calculated using three different methodologies that are presented in the ISO GUM 95 [3], which are the classic, numerical simulation and relative one.

By the classical method, the evaluation of measurement uncertainty estimation is done from the measurand definition steps; evaluating the standard uncertainties of coming sources; evaluation of combined standard uncertainty; calculation of effective degree of freedom and evaluation of expanded uncertainty. The evaluation of the estimated measurement uncertainty by numerical simulation method and by the relative uncertainty method adopt the same classical methodology in the evaluation of the coming sources of a measurand, however, to the calculus of the combined uncertainty the procedures described by Couto et al. [1] were used.

Figure 3 presents the results for the contributions to measurement uncertainty. As can be seen, the software allows for a graphic visualization of which factor is contributing most markedly to the final expanded uncertainty. Looking at sulfur measurements for the diesel fuel with data taken from a sample obtained for this study, it can be seen that the effect of the action of operators and the reference materials used in the analysis are considerable compared, but the calibration curve used showed a expressive contribution for the final uncertainty measurement.

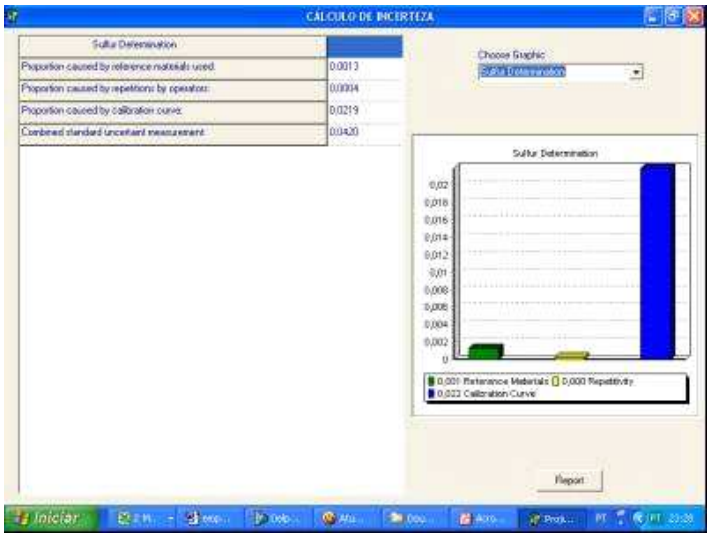

Figure 3. Final table of the software developed

Taking the flash point measurements into consideration, an experimental design was established and the analysis of repeatability and reprodutibility is showed on Figure 4. It is valid to emphasize that Figure 4 shows just one of processed data (automatic TAG), because the same methodology was implement to manual TAG, automatic and manual PENSKY. A similar procedure to sulfur uncertainty measurement was used to estimate flash point uncertainty measurement, but in this case the repeatability and reprodutibility standard deviations were used for the calculation of the combined standard uncertainty.

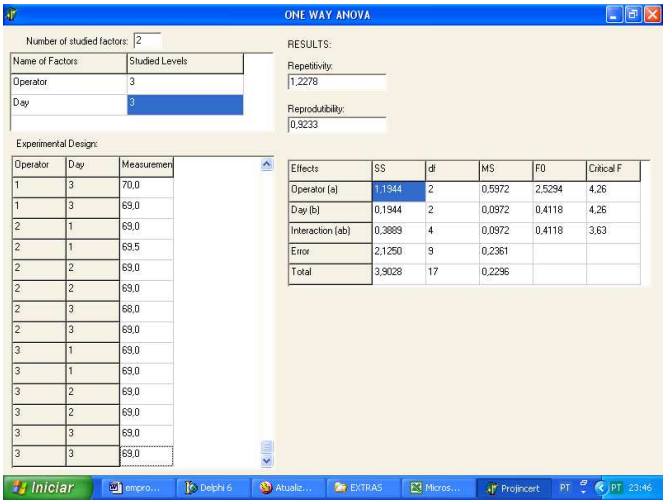

Figure 4. Experimental design applied to flash point of diesel fuel (Automatic TAG)

The result obtained by the laboratory for sulfur determination was (0.250 ± 0.084) mass %. To flash point, considering TAG flash point was obtained (69.1 ± 1.1) ºC and for PENSKY flash point, (75.4 ± 2.0) ºC. All the results are expressed using coverage factor (k) equal 2 for 95% of significance.

4. CONCLUSIONS

While estimating measurements of uncertainty is very important in assuring the reliability of measurement data, the estimation and interpretation process should also be easy and practical. In this respect, the software developed for this work served its purpose very well, supplying the final expanded uncertainty for sulfur and flash point measurements of diesel fuel, making it a useful tool for the analyst.

The data is inputted into this software, since it can also store data and generate reports on the results obtained, leading to faster access to specific information and making it easier to identify possible sources of error and start taking measures to minimize them.

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