CRITICAL METROLOGICAL EVALUATION OF FUEL ANALYSES BY MEASUREMENT UNCERTAINTY

Elcio Cruz de Oliveira

PETROBRAS TRANSPORTE S.A., Engineering Management, Av. Presidente Vargas, 328, 20091-060 Rio de Janeiro - RJ, Brazil
(✉ *elciooliveira@petrobras.com.br, +55 21 3211 9223*)

Abstract

It is now widely recognized that the evaluation of the uncertainty associated with a result is an essential part of any quantitative analysis. One way to use the estimation of measurement uncertainty as a metrological critical evaluation tool is the identification of sources of uncertainty on the analytical result, knowing the weak steps, in order to improve the method, when it is necessary. In this work, this methodology is applied to fuel analyses and the results show that the relevant sources of uncertainty are: beyond the repeatability, the resolution of the volumetric glassware and the blank in the analytical curve that are little studied.

Keywords: measurement uncertainty, critical metrological evaluation, resolution of the volumetric glassware, blank analytical, fuel analyses.

1. Introduction

Many important decisions are based on the results of chemical quantitative analysis; the results are used, for example, to estimate yields, to check materials against specifications or statutory limits, or to estimate monetary value. Users of the results of chemical analysis, particularly in those areas concerned with international trade, are coming under increasing pressure to eliminate the replication of effort frequently expended in obtaining them. In some sectors of Analytical Chemistry it is now a formal (frequently legislative) requirement for laboratories to introduce quality assurance measures to ensure that they are capable of and are providing data of the required quality [1].

As a consequence of these requirements, fuel industries are, for their part, coming under increasing pressure to demonstrate the quality of their results, and in particular to demonstrate their fitness for purpose, by giving a measure of the confidence that can be placed on the result. This is expected to include the degree to which a result would be expected to agree with other results and specifications, normally irrespective of the analytical methods used. One useful measure of this is measurement uncertainty [1].

The evaluation of uncertainty requires the analyst to look closely at all the possible sources of uncertainty. However, although a detailed study of this kind may require a considerable effort, it is essential that the effort expended should not be disproportionate. In practice a preliminary study will quickly identify the most significant sources of uncertainty and the value obtained for the combined uncertainty is almost entirely controlled by the major contributions. A good estimate of uncertainty can be made by concentrating the effort on the largest contributions [1].

In many cases, the declaration of compliance of a result of measurement is not clear. This is observed when there is a partial superposition of the expanded uncertainty of a quantity

with its limit of specification [2]. In these situations, one of the alternatives to clarify this dispute is to reduce the relevant sources of uncertainty.

The aim of this work is to make a critical metrological evaluation of some analyses of fuels by the powerful tool – measurement uncertainty, using the Guide of Uncertainty Measurement (GUM) approach [3]. From this approach, one is able to calculate quantitatively the degree of uncertainty – which has not been widely divulged in fuel analyses – and mainly, to understand better what are the weak steps of each method, stratifying the principal sources, in order "to attack" them if it is necessary to improve the methods.

In this work, the methodology is applied to and discussed in five different case studies in fuel analyses, which are very common and important, especially in Brazilian commercial field: level of anhydrous ethyl alcohol present in automotive gasoline [4]; level of hydrocarbons present in anhydrous ethyl alcohol fuel [5]; water in fuel oil by distillation [6]; flash point by Tag Closed Cup Tester in jet fuel [7] and sulfur in diesel oil by energy-dispersive X-ray fluorescence spectrometry [8].

2. Methodology

2.1. Uncertainty general theory

The uncertainty of a measurement is defined as "a parameter associated to the result of a measurement, which characterizes the dispersion of values that can be fundamentally attributed to a measurand" [9]. The result of a measurement is an information about the magnitude of a quantity, obtained experimentally and considered as the best estimate of the value of a measurand accompanied by all the sources of uncertainty that contribute to its propagation [10]. Decisions can be either correct or incorrect and are influenced by the uncertainty of measurement [11].

In the estimation of total uncertainty, it is necessary to deal separately with each source of uncertainty to know its contribution.

The combined standard uncertainty is calculated from the expansion of the Taylor series based on the Law of Propagation of Uncertainties (LPU). Supposing that the output quantity $\hat{y} = f(b_1, b_2, ..., b_n)$ depends on n input quantities $b_1, b_2,…,b_n$, where each b_i is described by a distribution of appropriate probability, the combined standard uncertainty assumes the form of (1), when taking into account that the quantities are correlated among themselves [3]:

$$u_c^2(\hat{y}) = \sum_{i=1}^{n}\left[\frac{\partial f}{\partial b_i}\right]^2 u_i^2 + 2\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\frac{\partial f}{\partial b_i}\frac{\partial f}{\partial b_j}u_i u_j r_{ij} . \tag{1}$$

From the effective degrees of freedom (number of terms in a sum less the number of restrictions to the terms of the sum), the required coverage factor, k, is calculated in the t-Student table, by (2):

$$v_{eff} = \frac{u_c^4(\hat{y})}{\sum\limits_{i=1}^{n}\dfrac{u_i^4(\hat{y})}{v_i}} . \tag{2}$$

And finally, the expanded uncertainty is given by (3):

$$U(\hat{y}) = u_c(\hat{y}) \times k \ \text{(for a determined level of confidence).} \tag{3}$$

2.2. Repeatability

The repeatability s_r or *Rep* indicates the variability observed within a laboratory, over a short period of time, using a single operator, item of equipment *etc.* s_r may be estimated within a laboratory or by inter-laboratory study [12]. In selecting factors for variation, it is important to ensure that the larger effects are varied where possible. The standard uncertainty arising from random effects is often measured from repeatability experiments and is quantified in terms of the standard deviation of the measured values. In practice, no more than about fifteen replicates need normally be considered, unless a high degree of precision is required [1].

Because a repeatability estimate is available from validation studies for the procedure as a whole, there is no need to consider all the repeatability contributions individually. They are therefore grouped into one contribution [1]. In some cases, the repeatability is substantially overestimated [13].

When the repeatability is derived from the method validation, it is generally expressed as relative standard deviation (% rsd) and this value can be used directly for the calculation of the combined standard uncertainty associated with the different repeatability terms [1].

Considering $\bar{b}$ to be a mean of each b_i, the repeatability can be calculated as $u_{b_i}/\sqrt{N}$, as described in [14, 15]:

$$\bar{b} = (b_1 + b_2 + b_3 + \cdots + b_N)/N$$

$$u_c^2(\bar{b}) = \left(\frac{\partial \bar{b}}{\partial b_1} \times u_{b_1}\right)^2 + \left(\frac{\partial \bar{b}}{\partial b_2} \times u_{b_2}\right)^2 + \left(\frac{\partial \bar{b}}{\partial b_3} \times u_{b_3}\right)^2 + \cdots + \left(\frac{\partial \bar{b}}{\partial b_N} \times u_{b_N}\right)^2$$

$$\partial \bar{b}/\partial b_1 = \partial \bar{b}/\partial b_2 = \partial \bar{b}/\partial b_3 = \cdots = \partial \bar{b}/\partial b_N = 1/N = \partial \bar{b}/\partial b_i$$

$$u_c^2(\bar{b}) = ((1/N) \times u_{b_1})^2 + ((1/N) \times u_{b_2})^2 + ((1/N) \times u_{b_3})^2 + \cdots + ((1/N) \times u_{b_N})^2$$

If, $u_{b_1} = u_{b_2} = u_{b_3} = \cdots = u_{b_N} = u_{b_i}$

$$u_c^2(\bar{b}) = N \times ((1/N) \times u_{b_i})^2$$

$$u_c(\bar{b}) = u_{b_i}/\sqrt{N}$$

2.3. Glassware volume: temperature, calibration certificate and resolution of the volumetric glassware

The volume of the solution contained in a volumetric flask is subject to three major sources of uncertainty, besides the repeatability (that in this work is evaluated from the method validation): temperature [16], calibration certificate and resolution of the volumetric glassware.

In measurement conditions, volumetric glassware may be used at an ambient temperature different from that at which it was calibrated. Gross temperature effects should be corrected, accounted for, but any uncertainty in the temperature of the liquid and glass should be considered. The uncertainty from this effect can be calculated from the estimate of the temperature range and the coefficient of the volume expansion. Generally, the volume expansion of the liquid is considerably larger than that of the flask, so only the former needs to be considered. Generally, it is provided in the laboratory temperature variation, ΔV, and what is required to calculate the uncertainty is the effect of the temperature on the volume of

the liquid, so this relation can be used: $\Delta V = V_0 \times \gamma \times \Delta T$, where ΔT is the possible temperature range, γ the coefficient of volume expansion of the liquid and V_0 is the liquid volume [17].

Resolution of a measuring system is the smallest change in the value of a quantity being measured by a measuring system that causes a perceptible change in the corresponding indication.

2.4. Recovery

With the objective of covering the uncertainties relative to systematic error – bias – of the method, estimates of recovery must also be considered. Barwick & Ellison describe several possibilities to estimate the uncertainty relative to recovery, including the analysis of certified reference materials (CRM), spiking and comparison with a reference method. Within these alternatives considered here, the utilization of CRM is discussed and applied in this work. The average recovery of the method is given by [18]:

$$\bar{R}_m = C_{standard} / \bar{C}_{method} ,\tag{4}$$

where $\bar{C}_{method}$ is the average of the results obtained using the method to be validated and $C_{standard}$ is the result from the certificate of the reference material. The uncertainty of recovery, $u(\bar{R}_m)$, is given by:

$$u(\bar{R}_m) = \bar{R}_m \sqrt{\frac{s_{method}^2}{n\bar{C}_{method}^2} + \left(\frac{u(C_{standard})}{C_{standard}}\right)^2} ,\tag{5}$$

where s_{method} is the standard deviation of the results obtained using the method, n is the number of replicates and $u(C_{standard})$ is the standard uncertainty associated with the CRM. The standard uncertainty of the CRM is utilized as standard deviation. If the recovery is significantly different from 1, we must use this correction for the result of the measurement.

A significance test is used to determine whether the mean recovery is significantly different from 1.0, based on the significance of the distance of the recovery in relation to the unit.

This test is based on the *t* test [19], whereby *n* observations, it is possible to assess whether an average of these results belongs to the population, when the true value is known.

$$|\mu - \bar{x}| \geq t_{critical} \times s / \sqrt{n}\tag{6}$$

$$|\mu - \bar{x}| \geq t_{critical} \times u\tag{7}$$

In this work, μ assumes 0 unity value and $\bar{x}$, the recovery ($\bar{R}_m$).

$$|1 - \bar{R}_m| \geq t_{critical} \times u(\bar{R}_m)\tag{8}$$

$$|1 - \bar{R}_m| / u(\bar{R}_m) \geq t_{critical}\tag{9}$$

This value is compared with the 2-tailed critical value $t_{critical}$, for $n - 1$ degrees of freedom at 95 % confidence (where *n* is the number of results used to estimate recovery). If *t* is greater or equal to the critical value, $t_{critical}$, then $\bar{R}_m$ is significantly different from 1, that is, besides the random errors, there are also systematic ones. In this case, a recovery correction factor is explicitly included in the calculation of the result and its uncertainty becomes a source of uncertainty.

2.5. Ordinary Least Squares (OLS) fit for the analytical curve

In the classical univariate calibration, n calibration points y define the analytical curve ($y = f(x)$), and the unknown quantity (x_0) is determined by the solution to the equation ($y_0 = f(x_0)$), where y_0 is the response for the unknown concentration. The most simple and widely used case is the following linear model: ($y = b_0 + b_1 x$), where the values of the independent variable x and uncertainty of the standards utilized in constructing the analytical curve are considered negligible, in addition to the variable of response y assumed to have randomly distributed errors of constant standard deviation – homocedasticity, Cochran test [19], after the outliers test, based on Grubbs approach. The unweighted linear regression is used to obtain estimates of the calibration parameters b_0 and b_1, derived from $x_0 = (y_0 - b_0)/b_1$.

Starting from n information points on the analytical curve and for p number of measurements to determine y_0, the standard uncertainty $\left(u_{x_0}\right)$ in x_0 is generally calculated from the (1) [1, 20 – 21]:

$$u_{c_0} = \frac{S}{a} \times \sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(c_0 - \bar{c})^2}{\sum\limits_{j=1}^{n}(c_j - \bar{c})^2}} \qquad (10)$$

Where, S – residual standard deviation; a – angular coefficient; p – number of measurements to determine c_0; n – number of measurements for the calibration; c_0 – determined analyte concentration; $\bar{c}$ – mean value of the different calibration standards (n number of measurements); j – index for the number of measurements to obtain the analytical curve.

Thus, based on (10), a calibration experiment of this type will give the most precise results when the measured instrument signal corresponds to a point close to the centroid of the regression line [19]. So, beyond the uncertainty of the sample it is also necessary to evaluate the analytical blank uncertainty [22].

However, the verification of linearity must be checked and the ANOVA test is the best one [21]. In order to perform the lack of fit test, the ANOVA statistical test should be carried out. The total variability of the responses is decomposed into the sum of the squares due to regression and the residual (about regression) sum of the squares and the latter is decomposed into lack of fit and pure error sums of the square. The former is concerned with deviation from linearity and the latter from repeated points. Replications of each calibration point give information about the inherent variability of the response measurements (pure error). If the replicates are repetitions of the same reading or obtained by successive dilutions, the residual variance σ_R^2 will tend to underestimate the variance σ^2 and the lack of fit test will tend to wrongly detect non-existence lack-of-fit [23]. The ANOVA table can be constructed from equations shown in Table 1.

Table 1. ANOVA table for OLS

Source of variation	Sum of squares, SS	Degree of freedom	Mean squares, MS	F
Regression, *REG*	SS_{REG}	1	MS_{REG}	MS_{REG}/MS_R
Residual, *R*	SS_R	$n - 2$	MS_R	
Lack of fit, *LOF*	SS_{LOF}	$k - 2$	MS_{LOF}	MS_{LOF}/MS_{PE}
Pure error, *PE*	SS_{PE}	$n - k$	MS_{PE}	
Total	SS_T	$n - 1$		

Where: k: the number of levels;
n: the total number of observations.

A significant MS_{REG} / MS_R ratio confirms that there is regression. If the ratio MS_{LOF} / MS_{PE} is higher than the critical level, the linear model appears to be inadequate [24]. A non-significant lack of fit indicates that there appears to be no reason to doubt the adequacy of the model and both the pure error and lack of fit mean the squares can be used as estimates of the variance σ^2.

3. Case studies

3.1. Case study 1: Level of anhydrous ethyl alcohol present in automotive gasoline (AEAC)

Presently, there is an increasing interest in adding oxygenated compounds to gasoline, because of their octane-enhancing and pollution-reducing capabilities [25].

In the United States, ethanol is sometimes added to gasoline but sold without an indication that it is a component. In several states, ethanol is added by law to a minimum level which is currently 5.9 %. In the European Union, 5 % ethanol can be infused with the common gasoline. Discussions are ongoing to allow 10 % blending of ethanol. Most gasoline sold in Sweden has 5–15 % ethanol added; also petrol blended ethanol, 85 % ethanol 15 % petrol is sold. In Brazil, the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP) requires that gasoline for automobile use has 25 % of ethanol added to its composition [26]. Legislation limits ethanol use to 10 % of gasoline in Australia.

This test method utilizes a salt water separation procedure.

3.2. Case study 2: Level of hydrocarbons present in anhydrous ethyl alcohol fuel (HYD)

Although fossil fuels have become the dominant energy resource for the modern world, alcohol has been used as a fuel throughout history [27].

Brazil was until recently the largest producer of alcohol fuel in the world, typically fermenting ethanol from sugarcane. Alcohol cars began to be sold in the Brazilian market in 1978 and became quite popular because of heavy subsidy, but in the 80's prices rose and gasoline regained the leading market share.

3.3. Case study 3: Water in fuel oil by distillation

Knowledge of the water content of petroleum products is important in the refining, purchase, sale, and transfer of products.

The amount of water may be used to correct the volume involved in the custody transfer of petroleum products and bituminous materials. The allowable amount of water may be specified in contracts [6].

The material to be tested is heated under reflux with a water-immiscible solvent, which co-distills with the water in the sample. The condensed solvent and water are continuously separated in a trap, the water settling in the graduated section of the trap and the solvent returning to the still section.

3.4. Case study 4: Flash point by Tag Closed Cup Tester in jet fuel

Flash point measures the tendency of the specimen to form a flammable mixture with air under controlled laboratory conditions. It is only one of a number of properties that shall be considered in assessing the overall flammability hazard of a material [7, 28]. Flash point can indicate the possible presence of highly volatile and flammable materials in a relatively

nonvolatile or nonflammable material. For example, an abnormally low flash point on a sample of jet fuel can indicate gasoline contamination [7].

The specimen is placed in the cup of the tester and, with the lid closed, heated at a slow constant rate. An ignition source is directed into the cup at regular intervals. The flash point is taken as the lowest temperature at which application of the ignition source causes the vapor above the specimen to ignite.

3.5. Case study 5: Sulfur in diesel fuel by energy dispersive X-ray fluorescence spectrometry

The quality of many petroleum products is related to the amount of sulfur present. There are also regulations promulgated in federal, state, and local agencies that restrict the amount of sulfur present in some fuels. Sulfur in diesel fuel damages the performance of after-treatment devices in two ways: first, it acts as a catalytic inhibitor; second, it is a precursor of sulfate [29].

The sample is placed in the beam emitted from an X-ray tube. The resultant excited characteristic X radiation is measured, and the accumulated count is compared with counts from previously prepared calibration samples to obtain the sulfur concentration in mass % and/or mg/kg. This test method provides a means of determining whether the sulfur content of petroleum or a petroleum product meets specification or regulatory limits.

4. Results and discussion

4.1. Level of anhydrous ethyl alcohol present in automotive gasoline (AEAC)

The mathematical model is:

$$AEAC,\ \% \left(V/V\right) = \left[\left(A - C\right)\times\left(B + C\right)/B\right] + 1, \qquad (11)$$

where *A* is the corrected final volume in the aqueous phase (NaCl reagent solution plus the anhydrous ethyl alcohol volume extracted from the sample), *B* is the sample volume and *C* the NaCl volume. All volumes are expressed in mL.

Table 2. Uncertainty evaluation of the level of anhydrous ethyl alcohol present in automotive gasoline (AEAC)

UNCERTAINTY EVALUATION OF THE LEVEL OF ANHYDROUS ETHYL ALCOHOL PRESENT IN AUTOMOTIVE GASOLINE (AEAC)										
	QUANTITY	Quantity value	Uncertainty value	Unit	Divisor	Distribution	Degree of freedom	Sensitivity coefficient, C_i	Standard uncertainty, $u(y_i)$ = $C_i \cdot u_i$	Uncertainty, $u(y_i)^2$	Contribution (%)
Sample volume (B)	Cylinder calibration certificate	50	0.03	mL	2.37	Normal	infinite	2.2	0.027895182	0.000778141	0
	Thermometer calibration certificate		3	ºC	1.73	Rectangular	infinite	0.121	0.21034025	0.044243021	1
	Cylinder resolution		1	mL	2.45	Triangular	infinite	2.2	0.898146239	0.806666667	15
NaCl solution (C)	Cylinder calibration certificate	50	0.04	mL	2.28	Normal	infinite	-1.8	-0.031523643	0.00099374	0
	Thermometer calibration certificate		3	ºC	1.73	Triangular	infinite	-0.14	-0.250974162	0.06298803	1
	Cylinder resolution		1	mL	2.45	Rectangular	infinite	-1.8	-0.734846923	0.54	10
Aqueous phase volume (A)	Cylinder calibration certificate	60	0.04	mL	2.37	Normal	infinite	2	0.067624683	0.004573098	0
	Thermometer calibration certificate		3	ºC	1.73	Rectangular	infinite	0.175	0.607603423	0.36918192	7
	Cylinder resolution		1	mL	2.45	Triangular	infinite	2	1.632993162	2.666666667	49
	Repeatability	1	0.048	-	1.00	Normal	infinite	21	1	1	18
						Normal	3284920	Combined standard uncertainty, u_c		2.34	100
								Coverage factor, *k*		2.00	
								Expanded uncertainty, *U*		4.7	% (V/V)
Result: AEAC = (21 ± 5) % (V/V)								Uncertainty (%):			22
The expanded uncertainty is reported based on a combined standard uncertainty, multiplied by a coverage factor of k = 2.00, providing a confidence level of approximately 95 %.											

Considering the non-correlated quantities, the combined standard uncertainties derived from (1), when applied to (11) are in (12) and (13), which are detailed in Table 2:

$$u_{AEAC}^2 = \left((\partial AEAC/\partial A) \times u_A\right)^2 + \left((\partial AEAC/\partial B) \times u_B\right)^2 + \left((\partial AEAC/\partial C) \times u_C\right)^2 + \left((\partial AEAC/\partial \mathrm{Rep}) \times u_{\mathrm{Rep}}\right)^2 \tag{12}$$

$$u_{AEAC}^2 = \left(\left((B+C)/B\right) \times u_A\right)^2 + \left(\left((A \times C) + C^2\right)/B^2 \times u_B\right)^2 + \left((A - B - 2 \times C)/B \times u_C\right)^2 + \left(\left[(A-C) \times (B+C)/B\right] + 1\right) \times u_{\mathrm{Rep}}\right)^2 \tag{13}$$

4.2. Level of hydrocarbons present in anhydrous ethyl alcohol fuel (HYD)

The mathematical model is:

$$HYD,\ \%\ (V/V) = \left(A \times (B+C)/B\right) + 1 \tag{14}$$

where A is the hydrocarbons volume, B is the sample volume and C is the NaCl volume. All volumes are expressed in mL.

Considering the non correlated quantities, the combined standard uncertainties derived from (1), when applied to (14) are in (15) and (16), which are detailed in Table 3:

$$u_{HYD}^2 = \left((\partial HYD/\partial A) \times u_A\right)^2 + \left((\partial HYD/\partial B) \times u_B\right)^2 + \left((\partial HYD/\partial C) \times u_C\right)^2 + \left((\partial HYD/\partial \mathrm{Rep}) \times u_{\mathrm{Rep}}\right)^2 \tag{15}$$

$$u_{HYD}^2 = \left((B+C)/B \times u_A\right)^2 + \left(-(A \times C)/B^2) - \times u_B\right)^2 + \left((A/B) \times u_C\right)^2 + \left((A \times (B+C)/B) + 1\right) \times u_{\mathrm{Rep}}\right)^2 \tag{16}$$

Table 3. Uncertainty evaluation of the level of hydrocarbons present in anhydrous ethyl alcohol (HYD)

UNCERTAINTY EVALUATION OF THE LEVEL OF HYDROCARBONS PRESENT IN ANHYDROUS ALCOHOL FUEL (HYD)										
	QUANTITY	Quantity value	Uncertainty value	Unit	Divisor	Distribution	Degree of freedom	Sensitivity coefficient, C_i	Standard uncertainty, $u(y_i) = C_i \cdot u_i$	Uncertainty, $u(y_i)^2$	Contribution (%)
Sample volume (B)	Cylinder calibration certificate	50.0	0.03	mL	2.37	Normal	infinite	-0.02	-0.000253593	6.43092E-08	0
	Thermometer calibration certificate		3	ºC	1.73	Retangular	infinite	-0.001	-0.001942668	3.77396E-06	0
	Cylinder resolution		1	mL	2.45	Triangular	infinite	-0.02	-0.008164966	6.66667E-05	0
NaCl solution (C)	Cylinder calibration certificate	50.0	0.04	mL	2.28	Normal	infinite	0.02	0.000350263	1.22684E-07	0
	Thermometer calibration certificate		3	ºC	1.73	Retangular	infinite	0.00	0.002650038	7.0227E-06	0
	Cylinder resolution		1	mL	2.45	Triangular	infinite	0.02	0.008164966	6.66667E-05	0
Hydrocarbons volume (A)	Cylinder calibration certificate	1.0	0.04	mL	2.28	Normal	infinite	2	0.070052539	0.004907358	0
	Thermometer calibration certificate		3	ºC	1.73	Retangular	infinite	0.153	0.530561803	0.281495827	9
	Cylinder resolution		1	mL	2.45	Triangular	infinite	2	1.632993162	2.666666667	87
Repeatability		1	0.333	-	1.00	Normal	infinite	1.0	0.333333333	0.111111111	4
						Normal	1303686	Combined standard uncertainty, u_c		1.75	100
								Coverage factor, k		2.00	
								Expanded uncertainty, U		3.5	% (V/V)
Result:	HYD = (3.0 ± 3.5) % (V/V)							Uncertainty (%):			117
The expanded uncertainty is reported based on a combined standard uncertainty, multiplied by a coverage factor of k = 2.00, providing a confidence level of approximately 95 %.											

4.3. Water in fuel oil by distillation

The mathematical model is:

$$Water,\ \%\ (V/V) = \left((A - B)/C\right) \times 100 \tag{17}$$

where A is the volume in the water receiver, B is the water in the solvent blank and C is the volume in the test sample. All volumes are expressed in mL.

Considering the non correlated quantities, the combined standard uncertainties derived from (1), when applied to (17) are in (18) and (19), which are detailed in Table 4:

$$u^2_{Water} = \left((\partial Water/\partial A)\times u_A\right)^2 + \left((\partial Water/\partial B)\times u_B\right)^2 + \left((\partial Water/\partial C)\times u_C\right)^2 + \left((\partial Water/\partial \text{Rep})\times u_{\text{Rep}}\right)^2 \tag{18}$$

$$u^2_{Water} = \left((100/C)\times u_A\right)^2 + \left((-100/C)\times u_B\right)^2 + \left((-(A-B)/C^2)\times u_C\right)^2 + \left(((A-B)/C)\times 100 \times u_{\text{Rep}}\right)^2 \tag{19}$$

Table 4. Uncertainty evaluation of water in fuel oil by distillation

UNCERTAINTY EVALUATION OF WATER IN FUEL OIL BY DISTILLATION										
QUANTITY		Quantity value	Uncertainty value	Unit	Divisor	Distribution	Degree of freedom	Sensitivity coefficient, C_i	Standard uncertainty, $u(y_i) = C_i * u_i$	Uncertainty, $u(y_i)^2$	Contribution (%)
Receiver water volume (A)	Receiver calibration certificate	0.25	0.0023	mL	2.00	Normal	infinite	1	0.00115	1.3225E-06	0
	Receiver resolution		0.1	mL	2.45	Triangular	infinite	1	0.040824829	0.00166667	42
	Thermometer calibration certificate		3	ºC	1.73	Rectangular	infinite	0.0004725	0.000818394	6.6977E-07	0
Receiver blank volume (B)	Receiver calibration certificate	0.00	0.0023	mL	2.00	Rectangular	infinite	-1	-0.00115	1.3225E-06	0
	Receiver resolution		0.1	mL	2.45	Triangular	infinite	-1	-0.040824829	0.00166667	42
	Thermometer calibration certificate		3	ºC	1.73	Rectangular	infinite	0.000000	0.000000	0.000000	0
Sample volume (C)	Cylinder calibration certificate	100.00	0.04	mL	2.00	Rectangular	infinite	-0.0025	-0.00005	2.5E-09	0
	Cylinder resolution		1	mL	2.45	Triangular	infinite	-0.0025	-0.001020621	1.0417E-06	0
	Thermometer calibration certificate		3	ºC	1.73	Rectangular	infinite	-0.0004725	-0.000818394	6.6977E-07	0
Repeatability		1	0.1	-	1.00	Normal	4	0.25	0.025	0.000625	16
						Normal	161	Combined standard uncertainty, u_c		0.06295524	10000%
								Coverage factor, k		2.02	
								Expanded uncertainty, U		0.13	% (V/V)
Result:	Water content = (0.25 ± 0.13) % V/V							Uncertainty (%):			51
The expanded uncertainty is reported based on a combined standard uncertainty, multiplied by a coverage factor of k = 2.02, providing a confidence level of approximately 95 %.											

In case studies 1, 2 and 3, the most relevant source of uncertainty is the resolution of the glassware. This source of uncertainty is very difficult to be treated, because the glassware construction follows international specifications.

4.4. Flash point by Tag Closed Cup Tester in jet fuel

The mathematical model is:

$$Corrected\ flash\ point\ (FP),°C = C + 0.25 \times (101.3 - p) \tag{20}$$

where C is the observed flash point, °C and p is the ambient barometric pressure, kPa.

Considering the non-correlated quantities, the combined standard uncertainties derived from (1), when applied to (20) are in (21) and (22), which are detailed in Table 5:

$$u^2_{FP} = \left((\partial FP/\partial C)\times u_C\right)^2 + \left((\partial FP/\partial p)\times u_p\right)^2 + \left((\partial FP/\partial CRM)\times u_{CRM}\right)^2 + \left((\partial FP/\partial \text{Calibration})\times u_{\text{Calibration}}\right)^2 + \left((\partial FP/\partial \text{Resolution})\times u_{\text{Resolution}}\right)^2 + \left((\partial FP/\partial \text{Rep})\times u_{\text{Rep}}\right)^2 \tag{21}$$

$$u^2_{FP} = (u_C)^2 + (-0.25 \times u_p)^2 + (u_{CRM})^2 + (u_{Calibration})^2 + (u_{Resolution})^2 + (u_{Repeatability})^2 \tag{22}$$

In this case study, the most relevant source of uncertainty is the repeatability. The repeatability used is derived from the ASTM. Probably, if the laboratory validates the method, and it uses its real value, this uncertainty source can be reduced.

Table 5. Uncertainty evaluation in flash point by tag closed cup tester in jet fuel

QUANTITY	Uncertainty value	Unit	Divisor	Distribution	Degree of freedom	Sensitivity coefficient, C_i	Standard uncertainty, $u(y_i) = C_i {}^* u_i$	Uncertainty, $u(y_i)^2$	Contribution (%)
UNCERTAINTY EVALUATION IN FLASH POINT BY TAG CLOSED CUP TESTER IN JET FUEL									
Certified Reference Material	0.3	ºC	2.00	Normal	infinite	1	0.15	0.0225	1.5
Resolution of the apparatus	0.5	ºC	3.46	Triangular	infinite	1	0.144337567	0.020833333	1.4
Temperature measuring device	0.02	ºC	2.00	Normal	infinite	1	0.01	0.0001	0.0
Calibration of the apparatus	0.2	ºC	2.00	Normal	infinite	1	0.1	0.01	0.7
Pressure	1	kPa	2.00	Normal	infinite	-0.25	-0.125	0.015625	1.0
Repeatability	1.2	ºC	1.00	Normal	infinite	1	1.2	1.44	95.4
				Normal	1097534	**Combined standard uncertainty, u_c**		1.228437354	100
						Coverage factor, k		2.00	
						Expanded uncertainty, U		2.5	ºC
Flash point = (40.0 ± 2.5)ºC						**Uncertainty (%):**			**6.1**
The expanded uncertainty is reported based on a combined standard uncertainty, multiplied by a coverage factor of k = 2.00, providing a confidence level of approximately 95 %.									

4.5. Sulfur in diesel fuel by energy dispersive X-ray fluorescence spectrometry

The mathematical model is:

$$Total\ sulfur\ content\ mass,\ \%\ (m/m) = (A - B) \times Recovery \tag{23}$$

where *A* is the sulfur concentration in the sample, % (m/m) and *B* is the sulfur concentration in the analytical blank, % (m/m).

Considering the non-correlated quantities, the combined standard uncertainties derived from (1), when applied to (23) are:

$$u_{Sulfur}^2 = \left((\partial Sulfur/\partial A) \times u_A\right)^2 + \left((\partial Sulfur/\partial B) \times u_B\right)^2 + \left((\partial Sulfur/\partial Recovery) \times u_{Recovery}\right)^2$$
$$+ \left((\partial Sulfur/\partial Rep) \times u_{Rep}\right)^2 \tag{24}$$

$$u_{Sulfur}^2 = \left(Recovery \times u_A\right)^2 + \left(-Recovery \times u_B\right)^2 + \left((A - B) \times u_{Recovery}\right)^2$$
$$+ \left((A\text{ - }B) \times Recovery \times u_{Rep}\right)^2 \tag{25}$$

Tables 6, 7 and 8 show the calibration results, the analysis results and the results of linearity and regression efficiency tests.

Table 6. Calibration results

Concentration (% m/m)	Signal 1	Signal 2	Signal 3
0.098	0.035	0.036	0.034
0.150	0.048	0.049	0.047
0.160	0.050	0.052	0.051
0.230	0.064	0.065	0.066
0.360	0.097	0.099	0.100
0.460	0.122	0.120	0.121
0.650	0.166	0.165	0.167

Table 7. Analysis results

	Signal 1	Signal 2	Signal 3
Blank	0.011	0.012	0.011
CRM	0.141	0.143	0.144
Sample	0.056	0.059	0.056

Table 8. Results of linearity and regression efficiency tests

Source of variation	Sum of squares, *SS*	Degree of freedom	Mean squares, *MS*	*F*
Regression, *REG*	0.040344514	1	0.040344514	**23424.613**
Residual, *R*	3.27239E-05	19	1.722313E-06	
Lack of fit, *LOF*	0.0000	5	3.21146E-06	**2.698**
Pure error, *PE*	0.0000	14	1.19048E-06	
Total	**0.040377238**	**20**		

$Y = 0.012163605 + 0.23696427 X$, R^2 = 0.99959 and explained variation = 99.92 %

The test statistic $F = 2.698$ is smaller than the critical $F_{0.05,\ 5,\ 14} = 2.958$ value. There is no significant evidence of lack of fit at $\alpha = 0.05$. Therefore, it can be concluded that the regression is satisfactorily explained by the linear model.

In order to evaluate the recovery effect, the certified value and its standard uncertainty given in CRM are 0.500 % and 0.0025 %, respectively.

CRM three replicates were analyzed and the concentration and its standard uncertainty were 0.555 % and 0.0038 %, respectively.

From (4), (5) and (9) respectively:

$$\overline{R}_m = 0.500/0.555 = 0.90215$$

$$u(\overline{R}_m) = 0.90215 \times \sqrt{\left((0.0038^2)/(3 \times 0.555^2)\right) + (0.0025/0.500)^2} = 0.00575$$

$$t = |1 - 0.90215|/0.00575 = 17.03$$

For a 95 % confidence level and 2 degrees of freedom, $t_{critical}$ is 4.30. As *t*, 17.03, is greater than the critical value, $t_{critical,}$ then $\overline{R}_m$ is significantly different from 1, that is, besides the random errors, there are also systematic ones. In this case, correction for recovery is necessary, besides being considered as a source of uncertainty.

Table 9 details the uncertainty.

Table 9. Uncertainty evaluation of the sulfur in diesel oil by energy dispersive X-ray fluorescence spectrometry

QUANTITY	Quantity value	Uncertainty value	Unit	Divisor	Distribution	Degree of freedom	Sensitivity coefficient, C_i	Standard uncertainty, $u(y_i) = C_i{}^*u_i$	Uncertainty, $u(y_i)^2$	Contribution (%)
UNCERTAINTY EVALUATION OF THE SULFUR IN DIESEL OIL BY ENERGY DISPERSIVE X-RAY FLUORESCENCE SPECTROMETRY										
Analytical curve - sample	**0.5507**	0.0035	% m/m	1.00	Normal	19	0.902149596	0.00315359	9.94513E-06	40.2
Analytical curve - blank	**-0.0035**	0.0040	% m/m	1.00	Normal	19	-0.902149596	-0.003568535	1.27344E-05	51.4
Repeatability	**1.0000**	0.0053	% m/m	1.00	Normal	5	0.173857868	0.000926858	8.59066E-07	3.5
Recovery	**0.9021**	0.0057	% m/m	1.00	Normal	2	0.19271512	0.00110732	1.22616E-06	5.0
					Normal	42	Combined standard uncertainty, u_c		0.004976424	100
							Coverage factor, *k*		2.06	
							Expanded uncertainty, *U*		0.010	% m/m
Result: Sulfur content = (0.174 ± 0.010) % m/m							**Uncertainty (%):**			**5.9**
The expanded uncertainty is reported based on a combined standard uncertainty, multiplied by a coverage factor of k = 2.06, providing a confidence level of approximately 95 %.										

In this case study, the most relevant source of uncertainty is the blank in the analytical curve. It is very interesting because in this situation, if the analytical blank is negligible, the measurement uncertainty is underestimated, reducing it wrongly to a half. This can be explained because the best adjustment in an analytical curve is the mean; however, this does not occur either at the beginning or at the end of the analytical curve.

5. Conclusions

Specific points of measurement uncertainty were provided in more detail in this paper, enabling the reader to use it more easily. From measurement uncertainty, it can be observed that if it is possible, mass is preferable to volume, because the latter has the influence of the temperature and the resolution of the glassware. It is recommended that the influence of the analytical blank be always evaluated, as it is noticed that in the case studied it is the greatest uncertainty source. The case studies presented allowed us to verify that the tool is really powerful to make a critical metrological evaluation of fuel analyses, detecting the major sources of uncertainty.

References

[1] EURACHEM/CITAC Guide. (2000). *Quantifying Uncertainty in Analytical Measurement.* EURACHEM/CITAC: Hungary.

[2] Oliveira, E.C., Aguiar, P.F. (2004). Evaluation of the uncertainty in measurement versus the limit of specification: qualitative and quantitative aspects of compliance. International Pipeline Conference.

[3] International Organization for Standardization (ISO). (1993*). Guide to the Expression of Uncertainty in Measurement*. ISO: Geneva. Switzerland.

[4] ABNT NBR 13992. (2008). Motor gasoline – Determinations of fuel anhydrous ethylic alcohol content.

[5] ABNT NBR 13993. (2002). Ethylic Alcohol – Determination of hydrocarbons content.

[6] ASTM D95 – 05. (2010). Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation. ASTM American Society for Testing and Materials.

[7] ASTM D56 – 05. (2005). Standard Test Method for Flash Point by Tag Closed Cup Tester. ASTM American Society for Testing and Materials.

[8] ASTM D4294 (2010). Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry. ASTM American Society for Testing and Materials.

[9] ISO/IEC Guide 99-12:2007. (2007). *International Vocabulary of Metrology. Basic and General Concepts and Associated Terms.* International Organization for Standardization: Geneva. Switzerland.

[10] Analytical Methods Committee. (1995). Analyst, 120, 2303–2008.

[11] White, R. (2011). The meaning of measurement in metrology. Accred. Qual. Assur., 16, 31–41.

[12] ISO 3534-2:2006. (2006). Statistics – Vocabulary and Symbols - Part 2: Probability and general statistical terms. International Organization for Standardization: Geneva. Switzerland.

[13] Rösslein, M., Rezzonico, S., Hedinger, R., Wolf, M. (2007). Repeatability: some aspects concerning the evaluation of the measurement uncertainty. Accred. Qual. Assur., 12, 425–434.

[14] Willink, R. (2009). The role of the sample standard deviation in the analysis of measurement data. Accred. Qual. Assur., 14, 353–358.

[15] Zieba, A. (2010). Effective number of observations and unbiased estimators of variance for autocorrelated data - an overview. *Metrology and Measurement Systems*, 17(1), 3–16.

[16] Lisowski, M. (2009). Issues of volume resistivity measurement of flat dielectric specimens and evaluation on uncertainty of the measurement results by approximate method at confidence level of 0.95. *Metrology and Measurement Systems*, 16(2), 233–248.

[17] Meyer, V.R., Pfohl, J., Winter, B. (2010). Calibration, handling repeatability, and the Maximum Permissible Error of single-volume glass instruments. *Accred. Qual. Assur.*, 15, 715–718.

[18] Oliveira, E.C., Aguiar, P.F. (2009). Methodology validation for evaluation of the uncertainty in the calibration curves better adjusted for second-degree polynomials. Quim. Nov, 32, 1655–1660.

[19] Miller, J.N., Miller, J.C. (2005). *Statistics and chemometrics for analytical chemistry*. New York.

[20] Miller, J.N. (1991). *Basic statistical methods for Analytical Chemistry. Part 2. Calibration and regression methods.* A review. Analyst, 116, 3–14.

[21] Vandeginste, B.G.M., Massart, D.L., Buydens, L.M.C., Jing, S., Lewi, P.J., Smeyers-Verbek, J. (1998). *Handbook of Chemometrics and Qualimetrics. Part B*. Elsevier. Amsterdam. Netherlands.

[22] Jiménez-Chacón, J., Alvarez-Prieto, M. (2010). *An approach to detection capabilities estimation of analytical procedures based on measurement uncertainty*. Accred. Qual. Assur., 15, 19–28.

[23] Chuí, Q.S.H. (2007). Uncertainties related to linear calibration curves: a case study for flame atomic absorption spectrometry. *J. Braz. Chem. Soc.*, 18, 424–430.

[24] Catelani, M., Zanobini, A., Ciani, L. (2010). Uncertainty interval evaluation using the Chi-square and Fisher distributions in the measurement process. *Metrology and Measurement Systems*, 17(2), 195–204.

[25] Doz, M.B.G., Bonatti, C.M., Sólimo, H.N. (2004). Water Tolerance and Ethanol Concentration in Ethanol-Gasoline Fuels at Three Temperatures. *Energy Fuels*, 18, 334–337.

[26] Pereira, R.C.C., Pasa, V.M.D. (2005). Effect of alcohol and copper content on the stability of automotive gasoline. *Energy Fuels*, 19, 426–432.

[27] Young, J.A. (2004). Lead dioxide. *J. Chem. Educ.*, 81, 1414–1418.

[28] Liaw, H., Gerbaud, V., Chiu, C. (2010). Flash point for ternary partially miscible mixtures of flammable solvents. *J. Chem. Eng. Data*, 55, 134–146.

[29] Kweon, C.-B., Okada, S., Stetter, J.C., Christenson, G. (2003). SAE Technol. Pap. Ser., 01-1899.