

ESTIMATION OF MEASUREMENT UNCERTAINTY FOR THE DETERMINATION OF THE TOTAL SULFUR CONTENT IN PETROLEUM AND PETROLEUM PRODUCTS IN UV-FLUORESCENT ANALYSIS

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Abstract

The measurement uncertainty was estimated for the determination of sulfur content in petroleum and petroleum products according to the recommendations of the EURACHEM/CITAC Guide and "Guide to the expression of uncertainty in measurement (GUM)". The major components contributing to their uncertainties were the amount of sulfur in the test sample and the method precision, based on the equation to calculate the measurand from the intermediate values. Consequently, the concentration of sulfur in the used CRM *ERM – EF 213* (certified value $9.1 \pm 0.8 \text{ mg kg}^{-1}$) with its expanded uncertainty was $9.8 \pm 4.0 \text{ mg kg}^{-1}$, which was acceptable to support the successful application of the analytical method. The method precision gave the largest contribution to the overall combined uncertainty of sulfur concentration.

Keywords: measurement uncertainty; sulfur concentration, petroleum products, UV-fluorescent analysis; method precision.

1. Introduction

The sulfur content in petroleum is a concern all over the world, because sulfur compounds are responsible for problems in storage, processing, transportation, and even the most important, the quality of the fuel products. Typical problems caused by sulfur compounds are catalyst poisoning and deactivation in processing, corrosion of equipment and the oxidation of sulfur compounds to SO_x when fuel combustion, which causes serious environmental pollution. In recent years, allowable sulfur levels in transportation fuel have been drastically lowered by government regulations to combat air pollution. A knowledge of desulfurization reactants and products is useful for the optimization of sulfur removal processes [1, 2].

Sulfur compounds, present in petroleum derivatives such as gasoline, kerosene, diesel fuel, and fuel oil, are corrosive and can inhibit the performance of additives in the final products [3, 4, 5].

Several methods for the determination of sulfur compounds have been reported, including colorimetric [6], titration [7], chromatographic [8], iodimetric [9, 10], X-ray fluorescence spectrometry [11, 12] and ultraviolet fluorescence [13].

In analytical chemistry one is familiar with applying Ordinary Least Squares Regression, based on the linear model $y = b_0 + b_1x + \varepsilon$, where y represents the response of the measurement system for the analyte content x , ε is the random deviation, and b_0 (intercept) and b_1 (slope) denote the regression coefficients used [14, 17]. The regression parameters are estimated from the n data pairs of the calibration data set $\{x_j, y_j\}$. Some regression assumption must be considered. The variable ε should have approximately a normal distribution whereby the conditions $(\varepsilon_i) = 0$ $\text{Var}(\varepsilon_i) = \sigma^2$ $\text{Cov}(\varepsilon_i, \varepsilon_j) = 0$ for $i \neq j$ are supposed [18].

The basic equations of measurement uncertainty for linear calibrations in chemical analysis is presented and comprehensively discussed in the Eurachem Guide, Appendix E of ref. [19].

In this work, the uncertainty of each step is calculated identifying which of them are relevant in the overall uncertainty. Particular attention is reserved to the critical problem of method recovery which often represents the greater contribution in global uncertainty.

2. Experimental

2.1. Chemicals and materials

Purity of Reagents – Reagent grade chemicals were used in tests. *Inert Gas* – Argon, high purity grade, 99.998 % purity, moisture 5 mg kg⁻¹ was used. *Oxygen* – High purity, 99.75 % purity, moisture 5 mg kg⁻¹, dried over molecular sieves. *Isooctane*, reagent grade was used (Merck). *Butyl Sulfide*, FW146.29, 21.92 % (m m⁻¹) S. Certificate Reference Material XR-626 Lot number T1100301003 manufacture by SPEX CertiPrep Group. *ERM – EF 213*, certified value 9.1 mg kg⁻¹, Certificate Reference Material manufacture by BAM – Germany.

2.2. Instrumentation

An Antek 9000 system was used for the detection of sulfur in petroleum and petroleum products. System features include: single detector operation; Windows-based software and PC control of instrumentation and data processing; massive method and data storage capability; monitored operating parameters that assure instrument performance; instrument control and operation from remote location, and:

Furnace – An electric furnace held at a temperature (1050±25°C) sufficient to pyrolyze all of the sample and oxidize sulfur to SO₂.

Combustion Tube – A quartz combustion tube constructed to allow the direct injection of the sample into the heated oxidation zone. The combustion tube has side arms for the introduction of oxygen and carrier gas. The oxidation section is large enough to ensure complete combustion of the sample.

Flow Control—The apparatus is equipped with flow controllers capable of maintaining a constant supply of oxygen and carrier gas.

Drier Tube—The apparatus is equipped with a mechanism for the removal of water vapor. It is accomplished with a membrane drying tube that utilizes a selective capillary action for water removal.

UV Fluorescence Detector—A qualitative and quantitative detector capable of measuring light emitted from the fluorescence of sulfur dioxide by UV light.

Microlitre Syringe – A microlitre syringe capable of accurately delivering 5 to 20-μL quantities.

Sample Inlet System – Either of two types of sample inlet systems was used.

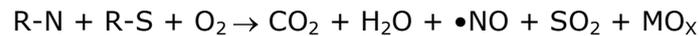
Direct Injection – A direct injection inlet system is capable of allowing the quantitative delivery of the material to be analyzed into an inlet carrier stream which directs the sample into the oxidation zone at a controlled and repeatable rate. A syringe drive mechanism which discharges the sample from the microlitre syringe at a rate of approximately 1 μL s⁻¹ is required.

Boat Inlet System – An extended combustion tube provides a seal to the inlet of the oxidation area and is swept by a carrier gas. The system provides an area to position the sample carrying mechanism (boat) at a retracted position removed from the furnace. The boat drive mechanism fully insert the boat into the hottest section of the furnace inlet. The sample boats and combustion tube are constructed of quartz. The combustion tube provides a cooling jacket for the area in which the retracted boat rests awaiting sample introduction from a microlitre syringe. A drive mechanism advances and withdraws the sample boat into and out of the furnace at a controlled and repeatable rate.

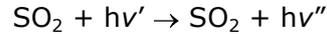
Refrigerated Circulator – An adjustable apparatus capable of delivering a coolant material at a constant temperature. *Strip Chart Recorder*, (optional). *Balance*, with a precision of ±0.01 mg (optional).

2.3 Description of procedures

The sample was vaporized and was combined with oxygen at a temperature in excess of 1000°C. Oxidation products include CO₂, H₂O, •NO, SO₂, and various other oxides (designated MO_x below). The conversion of chemically bound nitrogen to •NO (nitric oxide) and of sulfur to SO₂, (sulfur dioxide) is quantitative. The combustion gases were routed through a membrane drying system to remove all water and then to the detector module (s) for quantitation.



The SO_2 was exposed to ultraviolet radiation of a specific wavelength. This radiation was absorbed causing some electrons to shift to higher energy levels. As the electrons collapse back to their original levels, the excess energy was released in the form of light and was detected at specific wavelengths by a photomultiplier tube. This fluorescent emission was completely specific for sulfur and is proportional to the amount of sulfur in the original sample.



Sulfur calibration standards were analyzed to produce internal calibration curves. When the samples of unknown sulfur content were analyzed, the 9000 system automatically compared the raw sample data to the calibration curve to generate and report sulfur concentrations.

2.4 Sample preparation

The experimental investigations based exclusively on certified reference material (*Butyl Sulfide*, FW146.29, 21.92 % (m m⁻¹) S - Certificate Reference Material XR-626 Lot number T1100301003 manufacture by SPEX CertiPrep Group) and dilutions of it with isooctane (Merck).

The calibration curve (fig. 1) was performed by injecting CRM (*Butyl Sulfide*, FW146.29, 21.92 % (m m⁻¹) S - Certificate Reference Material XR-626 Lot number T1100301003 manufacture by SPEX CertiPrep Group), at different concentration levels. Then, the linearity of the UV-fluorescence method expressed as the initial concentration of sulfur in isooctane (1-25 mg kg⁻¹) was established. This method showed good linearity with regression coefficients $r^2 > 0.998$. Precision expressed as relative standard deviation (R.S.D) (<12%) and trueness estimated as relative error (<11) [20] at the studied concentration levels were satisfactory.

2.5 Estimation of measurement uncertainty

The uncertainty of measurement associated with the input estimates is evaluated according to either a "Type A" or a "Type B" method of evaluation. The Type A evaluation of standard uncertainty is the method of evaluating the uncertainty by the statistical analysis of a series of observations. In this case the standard uncertainty is the experimental standard deviation of the mean that follows from an averaging procedure or an appropriate regression analysis. The Type B evaluation of standard uncertainty is the method of evaluating the uncertainty by means other than the statistical analysis of a series of observations.

Assume that the repeatedly measured input quantity X_i is the quantity Q . With n statistically independent observations ($n > 1$), the estimate of the quantity Q is \bar{q} , the arithmetic mean or the average of the individual observed values q_j ($j=1,2,\dots,n$).

$$\bar{q} = \frac{1}{n} \sum_{j=1}^n q_j$$

The uncertainty of measurement associated with the estimate \bar{q} is evaluated according to one of the following methods:

(a) An estimate of the variance of the underlying probability distribution is the experimental variance $s^2(q)$ of values q_j that is given by

$$s^2(q) = \frac{1}{n-1} \sum_{j=1}^n (q_j - \bar{q})^2$$

Its (positive) square root is termed experimental standard deviation. The best estimate of the variance of the arithmetic mean \bar{q} is the experimental variance of the mean given by

$$s^2(\bar{q}) = \frac{s^2(q)}{n}$$

Its (positive) square root is termed experimental standard deviation of the mean. The standard uncertainty $u(\bar{q})$ associated with the input estimate \bar{q} is the experimental standard deviation of the mean

$$u(\bar{q}) = s(\bar{q})$$

Type B evaluation of standard uncertainty

The Type B evaluation of standard uncertainty is the evaluation of the uncertainty associated with an estimate x_i of an input quantity X_i by means other than the statistical analysis of a series of observations. The standard uncertainty $u(x_i)$ is evaluated by scientific judgment based on all available information on the possible variability of X_i . Values belonging to this category may be derived from:

- Previous measurement data;
- Experience with or general knowledge of the behavior and properties of relevant materials and instruments;
- Manufacturer's specifications;
- Data provided in calibration and other certificates;
- Uncertainties assigned to reference data taken from handbooks.

CALCULATION OF THE STANDARD UNCERTAINTY OF THE OUTPUT ESTIMATE

For uncorrelated input quantities the square of the standard uncertainty associated with the output estimate y is given by

$$u^2(y) = \sum_{i=1}^N u_i^2(y)$$

The quantity $u_i(y)$ ($i = 1, 2, \dots, N$) is the contribution to the standard uncertainty associated with the output estimate y resulting from the standard uncertainty associated with the input estimate x_i

$$u_i(y) = c_i u(x_i)$$

where c_i is the sensitivity coefficient associated with the input estimate x_i , i.e. the partial derivative of the model function f with respect to X_i , evaluated at the input estimates x_i ,

$$c_i = \frac{\partial f}{\partial x_i} = \left. \frac{\partial f}{\partial X_i} \right|_{X_1=x_1 \dots X_N=x_N}$$

The sensitivity coefficient c_i describes the extent to which the output estimate y is influenced by variations of the input estimate x_i . It can be evaluated from the model function f or by using numerical methods, i.e. by calculating the change in the output estimate y due to a change in the input estimate x_i of $+u(x_i)$ and $-u(x_i)$ and taking as the value of c_i the resulting difference in y divided by $2u(x_i)$. Sometimes it may be more appropriate to find the change in the output estimate y from an experiment by repeating the measurement at e.g. $x_i \pm u(x_i)$.

Whereas $u(x_i)$ is always positive, the contribution $u_i(y)$ according to equation (4.2) is either positive or negative, depending on the sign of the sensitivity coefficient c_i . The sign of $u_i(y)$ has to be taken into account in the case of correlated input quantities.

If the model functions f is a sum or difference of the input quantities X_i ,

$$f(X_1, X_2, \dots, X_N) = \sum_{i=1}^N p_i X_i$$

the output estimate according to equation (2.2) is given by the corresponding sum or difference of the input estimates:

$$y = \sum_{i=1}^N p_i X_i$$

whereas the sensitivity coefficients equal p_i and equation (4.1) converts to

$$u^2(y) = \sum_{i=1}^N p_i^2 u^2(x_i)$$

If the model function f is a product or quotient of the input quantities X_i

$$f(X_1, X_2, \dots, X_N) = c \prod_{i=1}^N X_i^{p_i}$$

the output estimate again is the corresponding product or quotient of the input estimates

$$y = c \prod_{i=1}^N X_i^{p_i}$$

The sensitivity coefficients equal $p_i y/x_i$ in this case and an expression analogous to equation (4.6) is obtained from equation (4.1), if relative standard uncertainties $w(y) = u(y)/|y|$ and $w(x_i) = u(x_i)/|x_i|$ are used,

$$w^2(y) = \sum_{i=1}^N p_i^2 w^2(x_i)$$

If two input quantities X_i and X_k are correlated to some degree, i.e. if they are mutually dependent in one way or another, their covariance also has to be considered as a contribution to the uncertainty. The ability to take into account the effect of correlations depends on the knowledge of the measurement process and on the judgement of mutual dependency of the input quantities. In general, it should be kept in mind that neglecting correlations between input quantities can lead to an incorrect evaluation of the standard uncertainty of the measurand.

The covariance associated with the estimates of two input quantities X_i and X_k may be taken to be zero or treated as insignificant if:

- (a) The input quantities X_i and X_k are independent, for example, because they have been repeatedly but not simultaneously observed in different independent experiments or because they represent resultant quantities of different evaluations that have been made independently, or if
- (b) Either of the input quantities X_i and X_k can be treated as constant, or if
- (c) Investigation gives no information indicating the presence of correlation between the input quantities X_i and X_k .

Sometimes correlations can be eliminated by a proper choice of the model function.

The uncertainty analysis for a measurement - sometimes called the uncertainty budget of the measurement - should include a list of all sources of uncertainty together with the associated standard uncertainties of measurement and the methods of evaluating them. For repeated measurements the number n of observations also has to be stated. For the sake of clarity, it is recommended to present the data relevant to this analysis in the form of a table. In this table all quantities should be referenced by a physical symbol X_i or a short identifier. For each of them at least the estimate x_i , the associated standard uncertainty of measurement $u(x_i)$, the sensitivity coefficient c_i and the different uncertainty contributions $u_i(y)$ should be specified. The dimension of each of the quantities should also be stated with the numerical values given in the table.

Table 1. Schematic of an ordered arrangement of the quantities, estimates, standard uncertainties, sensitivity coefficients and uncertainty contributions used in the uncertainty analysis of a measurement

Quantity	Estimate	Standard uncertainty	Sensitivity coefficient	Contribution to the standard uncertainty
X_{1r}	x_i	$u(x_i)$	c_i	$u_i(y)$
X_{1r}	x_1	$u(x_1)$	c_1	$u_1(y)$
X_2	x_2	$u(x_2)$	c_2	$u_2(y)$
\vdots	\vdots	\vdots	\vdots	\vdots
X_{nr}	x_n	$u(x_n)$	c_n	$u_n(y)$
Y	y			$u(y)$

A formal example of such an arrangement is given as Table 1 applicable for the case of uncorrelated input quantities. The standard uncertainty associated with the measurement result $u(y)$ given in the bottom right corner of the table is the root sum square of all the uncertainty contributions in the outer right column. The grey part of the table is not filled in.

EXPANDED UNCERTAINTY OF MEASUREMENT

Within EAL it has been decided that calibration laboratories accredited by members of the EAL shall state an expanded uncertainty of measurement U , obtained by multiplying the standard uncertainty $u(y)$ of the output estimate y by coverage factor k ,

$$U = ku(y)$$

In cases where a normal (Gaussian) distribution can be attributed to the measurand and the standard uncertainty associated with the output estimate has sufficient reliability, the standard coverage factor $k = 2$ shall be used. The assigned expanded uncertainty corresponds to a coverage probability of approximately 95%. These conditions are fulfilled in the majority of cases encountered in calibration work. The assumption of a normal distribution cannot always be easily confirmed experimentally. However, in the cases where several (i.e. $N \geq 3$) uncertainty components, derived from well-behaved probability distributions of independent quantities, e.g. normal distributions or rectangular distributions, contribute to the standard uncertainty associated with the output estimate by comparable amounts, the conditions of the Central Limit Theorem are met and it can be assumed to a high degree of approximation that the distribution of the output quantity is normal.

The reliability of the standard uncertainty assigned to the output estimate is determined by its effective degrees of freedom. However, the reliability criterion is always met if none of the uncertainty contributions is obtained from a Type A evaluation based on less than ten repeated observations. If one of these conditions (normality or sufficient reliability) is not fulfilled, the standard coverage factor $k = 2$ can yield an expanded uncertainty corresponding to a coverage probability of less than 95%. In these cases, in order to ensure that a value of the expanded uncertainty is quoted corresponding to the same coverage probability as in the normal case, other procedures have to be followed. The use of approximately the same coverage probability is essential whenever two results of measurement of the same quantity have to be compared, e.g. when evaluating the results of an inter-laboratory comparison or assessing compliance with a specification.

Even if a normal distribution can be assumed, it may still occur that the standard uncertainty associated with the output estimate is of insufficient reliability. If, in this case, it is not expedient to increase the number n of repeated measurements or to use a Type B evaluation instead of the Type A evaluation of poor reliability. For the remaining cases, i.e. all cases where the assumption of a normal distribution cannot be justified, information on the actual probability distribution of the output estimate must be used to obtain a value of the coverage factor k that corresponds to a coverage probability of approximately 95% [21].

3. RESULTS AND DISCUSSION

3.1. Specification of the measurand

It is necessary to define what is being measured and express quantitatively the relationship among the measurands in the first step. The concentration of the sulfur (C_{sulfur}) in the test sample (*EF 213*, certified value 9.1 mg kg^{-1} , Certificate Reference Material manufacture by BAM – Germany) was calculated by a simple mathematical model:

$$C_{\text{sulfur}} = \frac{C_0}{d} \text{ (mg kg}^{-1}\text{)} \quad (1)$$

where C_0 is the concentration of the sulfur in the test sample and d is the relative density of the test sample.

3.2. Identifying uncertainty sources

The relevant uncertainty sources are shown in the cause and effect diagram (Fig. 1).

From Eq. (1) C_{sulfur} was associated with C_0 and relative density d of the test sample (its uncertainty effect on the sulfur concentration is negligible). C_0 was calculated from calibration curve. The cause and effect diagram was expanded with the added correction factor, method precision. Moreover, the working standard solution was considered as another uncertainty source of C_0 . Also, the repeatability of measurement and the variation of the solvent volume due to temperature change overlap with the uncertainty of the method precision, where those factors are already covered. The repeatability and the temperature effect of the volumetric apparatus for the preparation of both the stock solution and the intermediate standard solution were regarded as contributors to the estimation of the measurement uncertainty since the solutions were made beforehand.

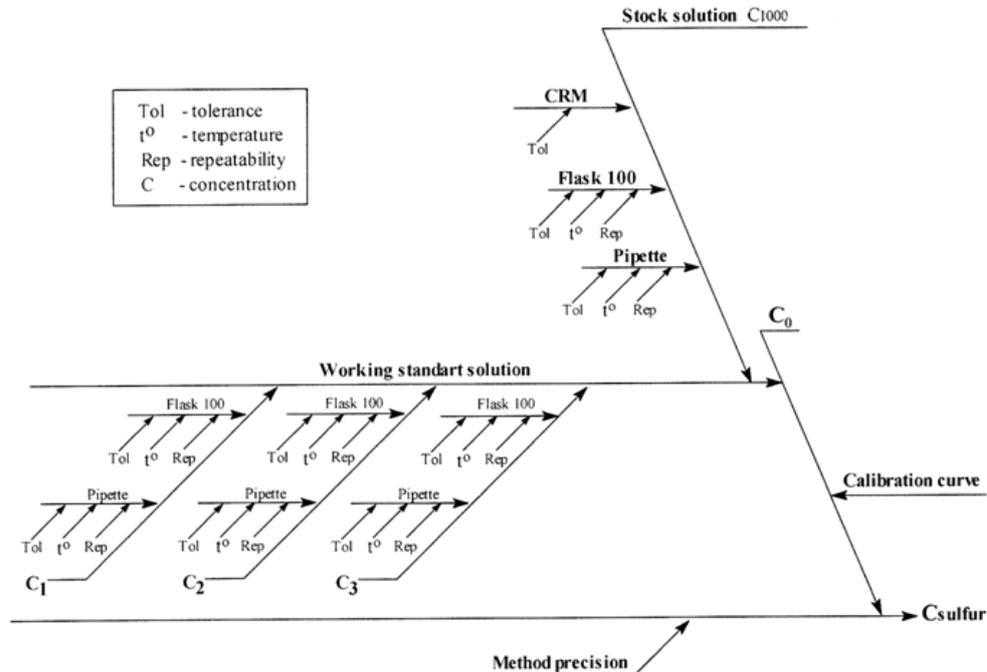


Fig. 1 Expanded cause and effect diagram

3.3. Quantifying uncertainty

3.2.1. Sulfur content (C_{sulfur})

In order to create the RSU of C_{sulfur} ($U_r(C_{\text{sulfur}})$), the two uncertainty components, one from the preparation of the working standard solution and the other from the calibration curve, were combined as follows:

$$U_r(C_0) = \sqrt{U_r^2(Std) + U_r^2(Cal)} = \sqrt{U_r^2(Std) + \left(\frac{U(Cal)}{C_0}\right)^2} = 0.085 \quad (2)$$

$$U_r(Std) = \sqrt{U_i^2(Stock) + 4 \cdot \left(\frac{U(Flask_{100})}{100}\right)^2 + 4 \cdot \left(\frac{U(Pipette)}{1}\right)^2 + U_r(C_{25})^2 + U_r(C_5)^2 + U_r(C_1)^2} = 0.065 \quad (3)$$

$$U_r(Stock) = \sqrt{\left(\frac{U_r(CRM)}{CRM}\right)^2 + \left(\frac{U_r(Flask_{100})}{100}\right)^2 + \left(\frac{U_r(Pipette)}{1}\right)^2} = 0.011 \quad (4)$$

$$U_{(Flask_{100})} = \sqrt{U_{(tol)}^2 + U_{(temp)}^2 + U_{(rep)}^2} = 0.24 \quad (5)$$

$$U_{(tol_{100})} = \frac{0.1}{\sqrt{3}} = 0.06 \text{ ml} \quad (6)$$

$$U_{(temp_{100})} = \frac{0.4}{\sqrt{3}} = 0.23 \text{ ml} \quad (7)$$

$$U_{(rep_{100})} = \frac{0.0208}{\sqrt{10}} = 0.0066 \text{ ml} \quad (8)$$

$$U_{(CRM)} = \frac{657}{219100} = 0.003 \text{ mg kg}^{-1} \quad (9)$$

$$U_{Pipette} = \sqrt{U_{(tol_1)}^2 + U_{(temp_1)}^2 + U_{(rep_1)}^2} = \pm 0.0099 \text{ ml} \quad (10)$$

$$U_{(tol_1)} = 0.004 \text{ ml} \quad (11)$$

$$U_{(temp_1)} = 0.0023 \text{ ml} \quad (12)$$

$$U_{(rep_1)} = 0.0081 \text{ ml} \quad (13)$$

$$U_r(C_{25}) = 0.06 \quad (14)$$

$$U_r(C_5) = 0.011 \quad (15)$$

$$U_r(C_1) = 0.0023 \quad (16)$$

where $u_r(\text{Std})$ is the relative standard uncertainty of the working standard solution, $u_r(\text{Cal})$ is that of the calibration curve and the $u(\text{Cal})$ is the standard uncertainty of the calibration curve. For the calculation of $u_r(\text{Std})$, following uncertainties were considered: uncertainty in the preparation of the stock solution, $u_r(\text{Stock})$; uncertainty in the use of pipette to make the calibrators and the intermediate standard solution $u(\text{Pipette})$; uncertainty in the use of Flask 100 to make the stock and working standard solutions $u(\text{Flask100})$; uncertainty from the certified reference material $U(\text{CRM})$.

The uncertainty of tolerance of the glassware was estimated using results obtained from the manufacturer's certificates and the function of the rectangular distribution. Since the glassware had been calibrated at 20 °C but the temperature of our laboratory is adjusted at 20 ± 5 °C, the effect of temperature on the volume of the isooctane was also considered using the coefficient of the expansion of isooctane, 1×10^{-3} . The uncertainty of repeatability of the glassware was calculated using the standard deviation from ten measurements.

As we prepared three solutions from stock solution of CRM (*Butyl Sulfide*, FW146.29, 21.92 % (m m⁻¹) S - Certificate Reference Material XR-626 Lot number T1100301003 manufacture by SPEX CertiPrep Group), combining the values with the uncertainty calculated for the concentration of the stock solution gives an uncertainty in the concentration of the dilute working standards $u_r(C_1)$, $u_r(C_5)$, $u_r(C_{25})$.

The calibration curve was given by $A_j = c_i \cdot B_1 + B_0$ where A_j is the j th measurement of the peak area ratio of the i th calibration standard, c_i is the amount of the i th calibration standard and B_1 and B_0 are the slope and the intercept of the calibration curve, respectively. The three calibration standards were measured five times each (Fig. 2), providing the results of the mean values of the different calibration standards, slopes and intercepts for sulfur content.

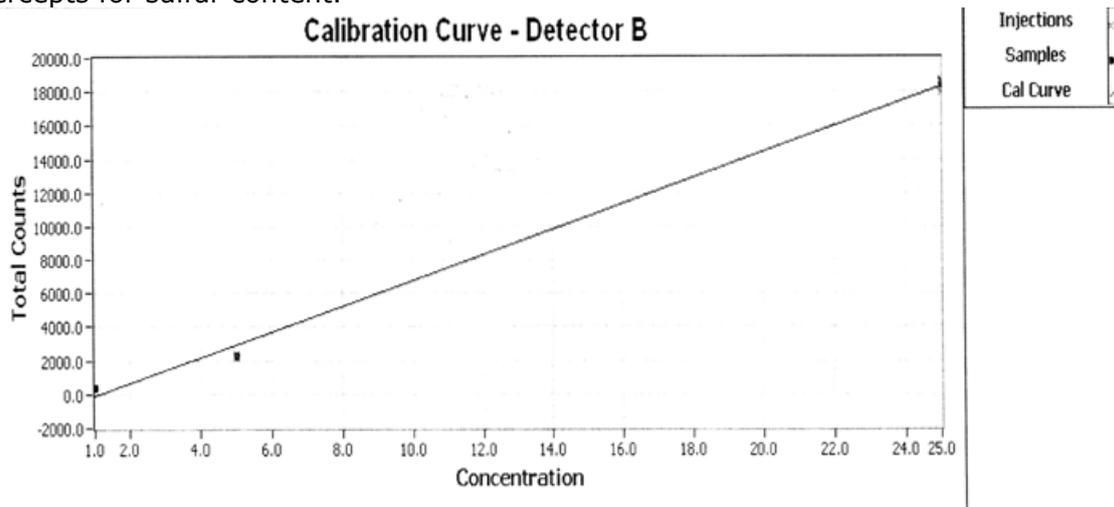


Fig. 2 Calibration curve of sulfur concentration in the range 0-25 mg kg⁻¹ ($r = 0.998$).

The *ERM - EF 213* (certified value 9.1 mg kg⁻¹, Certificate Reference Material manufacture by BAM - Germany) was analyzed, leading to c_0 of 8.8 mg kg⁻¹. Therefore, the uncertainty $u(\text{Cal})$ of sulfur content was given by as follows:

$$U(\text{Cal}) = \frac{S}{B_1} \sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(C_0 - C)^2}{S_{xx}}} = 0.48 \text{ mg kg}^{-1} \quad (17)$$

with the residual standard deviation S given by

$$S = \sum_{j=1}^n \frac{[A_j - (B_0 + B_1 \cdot C_j)]^2}{n-2} = 703.3 \quad (18)$$

and

$$S_{xx} = \sum_{j=1}^n (C_j - C)^2 = 330.6 \quad (19)$$

where B_1 is the slope, p is the number of measurements to determine c_0 , n is the number of measurement for the calibration, c_0 is the amount of sulfur in the test sample (ERM – EF 213), c is the mean value of the different calibration standards (n number of measurements), i is the index for the number of calibration standards and j is the index for the number of measurements to obtain the calibration curve.

3.2.2. Method precision

The uncertainty of the method precision for sulfur content was calculated using the pooled standard deviation (s_p) given by

$$S_p = \sqrt{\frac{\sum_{i=1}^N \nu_i \times s_i^2}{\sum_{i=1}^N \nu_i}} \quad (20), \text{ and}$$

$$u = \frac{S_p}{\sqrt{m}} \quad (21)$$

where ν_i is the degree of freedom of the i th sample, s_i is the standard deviation of the i th sample and m is the number of independent measurements. The results of evaluation of the method precision for sulfur content with their SU and RSU are shown in Table 2. The uncertainty $u_r(f_{\text{precision}})$ of sulfur content was 0.19.

Table 2. Results of the evaluation of method precision.

CRM, mg kg ⁻¹	Day	Mean	Standard deviation	Degrees of freedom	SU (mg kg ⁻¹)	RSU
9.1±0.8	1	8.95	0.50	5	0.20	0.022
	2	8.63	0.51	2	0.30	0.030
	3	8.63	0.40	2	0.23	0.030
	4	8.67	0.65	2	0.38	0.040
	5	8.90	0.70	2	0.40	0.040

3.4. Calculating the overall combined uncertainty

The sulfur content in the test sample (ERM – EF 213) was calculated using equation (1) as follows:

$$C_{\text{sulfur}} = \frac{C_0}{d} = \frac{8.8}{0.9} = 9.8 \text{ mg kg}^{-1}$$

The overall combined uncertainty was given by

$$U_c(C_{\text{sulfur}}) = C_{\text{sulfur}} \cdot \sqrt{U_r^2(C_0) + U_r^2(\text{Prec})} = 2 \text{ mg kg}^{-1} \quad (22)$$

3.5. Calculating the degrees of freedom

The degree of freedom of sulfur concentration was approximated by the Welch-Satterthwaite formula:

$$v_{\text{eff}} = \frac{u_c^4(y)}{\sum_{i=1}^N u_i^4(y)/v_i} = 44 \quad (23)$$

where v_{eff} is the effective degree of freedom; $u_c(y)$ is the combined standard uncertainty; $u_i(y)$ is the individual standard uncertainty, and v_i is the degree of freedom of $u_i(y)$.

3.6. Calculating the expanded uncertainty

The degree of freedom of sulfur concentration was large enough to consider the coverage factor (k) as 2 at the 95% significance level. Thus, the expanded uncertainty of sulfur concentration in the test sample (ERM – EF 213) was given by

$$U(C_{\text{sulfur}}) = 2 \times 2 = 4 \text{ mg kg}^{-1}$$

Therefore, the sulfur concentration in the test sample with its expanded uncertainty was $9.8 \pm 4.0 \text{ mg kg}^{-1}$.

4. Conclusion

This study illustrates the application of cause-and-effect analysis to uncertainty estimation in UV-fluorescent technique.

Where compare our result ($9.8 \pm 4.0 \text{ mg kg}^{-1}$), obtained by application of equation 1, with the certified of reference material that presents a sulfur concentration as $9.1 \pm 0.8 \text{ mg kg}^{-1}$, we concluded that analytical method is appropriate, sensitive and provides a global estimation of the uncertainty.

The estimation of the uncertainty components showed to be a suitable tool for the experimental design in order to obtain a small uncertainty in the analytical result.

In this experiment, the major contribution to the uncertainty budget was found to be the method precision, while the contribution from the uncertainty associated with the sulfur concentration in the test sample was insignificant.

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