Talanta 105 (2013) 360–365

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Estimation of measurement uncertainty arising from manual sampling of fuels

Dimitrios Theodorou *[,1], Nikolaos Liapis, Fanourios Zannikos

National Technical University of Athens, School of Chemical Engineering, Laboratory of Fuels and Lubricants Technology, Iroon Polytechneiou 9, Athens 15780, Greece

ARTICLE INFO

Article history:
Received 3 June 2012
Received in revised form
14 October 2012
Accepted 18 October 2012
Available online 29 October 2012

Keywords:
Uncertainty
Sampling
Fuel
Classical ANOVA
Robust ANOVA
Range statistics

ABSTRACT

Sampling is an important part of any measurement process and is therefore recognized as an important contributor to the measurement uncertainty. A reliable estimation of the uncertainty arising from sampling of fuels leads to a better control of risks associated with decisions concerning whether product specifications are met or not. The present work describes and compares the results of three empirical statistical methodologies (classical ANOVA, robust ANOVA and range statistics) using data from a balanced experimental design, which includes duplicate samples analyzed in duplicate from 104 sampling targets (petroleum retail stations). These methodologies are used for the estimation of the uncertainty arising from the manual sampling of fuel (automotive diesel) and the subsequent sulfur mass content determination. The results of the three methodologies statistically differ, with the expanded uncertainty of sampling being in the range of 0.34–0.40 mg kg^{-1}, while the relative expanded uncertainty lying in the range of 4.8–5.1%, depending on the methodology used. The estimation of robust ANOVA (sampling expanded uncertainty of 0.34 mg kg^{-1} or 4.8% in relative terms) is considered more reliable, because of the presence of outliers within the 104 datasets used for the calculations. Robust ANOVA, in contrast to classical ANOVA and range statistics, accommodates outlying values, lessening their effects on the produced estimates. The results of this work also show that, in the case of manual sampling of fuels, the main contributor to the whole measurement uncertainty is the analytical measurement uncertainty, with the sampling uncertainty accounting only for the 29% of the total measurement uncertainty.

1. Introduction

The aim of sampling is to obtain a small portion of material (sample) from a selected system (sampling target) within a container which is representative of the material in that system [1,2]. The sampling process should ensure that the sample is an unbiased reflection of the composition of the sampling target [1]. Representative samples of petroleum and petroleum products are required for the determination of their chemical and physical properties, which are often used to establish compliance with commercial and regulatory specifications [2].

When a measurement result is compared with specified limits in order to make a decision relating to conformance or compliance, it is very likely that measurement uncertainty will have implications for the interpretation of the result. Not accounting for the uncertainty (deterministic approach) may lead to incorrect decisions i.e. false positive or false negative classifications that may have financial, health, environmental or other consequences [3,4]. Fig. 1 shows the four situations apparent for a case of compliance with an upper limit and the conclusions drawn under the probabilistic and deterministic approach (assuming that an upper limit is set with no allowance for uncertainty). EURACHEM/ CITAC Guide "Use of uncertainty information in compliance assessment" [5] covers the above matters extensively.

Sampling becomes extremely important when considering the uncertainty of measurement. Until recently a "metrological gap" existed between analysts and end-users concerning the interpretation of measurement results and their associated uncertainties. Analysts concentrated on the analytical measurement process and estimated the uncertainty of the measurand of the sample received at the laboratory while the end user naturally interpreted the measurement result together with its uncertainty in order to characterize the sampling target as a whole [7,8]. Therefore, the end user needs to know a precise estimate of an uncertainty that includes the uncertainty caused by sampling i.e. the combined uncertainty from sampling and analysis [7,9,10]. Reliable estimations of the uncertainties of fuel sampling and analysis are important as they are associated with the application of legal requirements and the identification of events of cross contamination of incompatible fuels and fuel adulteration.

* Corresponding author. Tel./fax: +30 21 0652 5976.
E-mail address: dtheodoro@teemail.gr (D. Theodorou).
[1] Permanent Address: 57a Parnassou Street, 15234 Halandri, Athens, Greece.

0039-9140/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.10.058

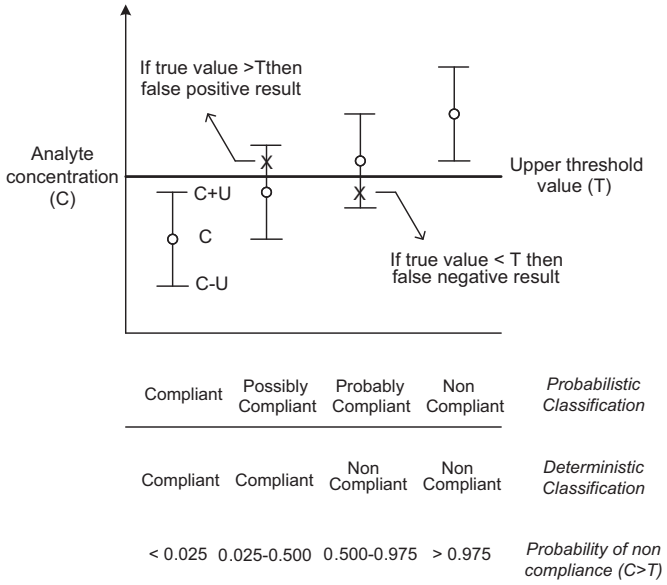

Fig. 1. Deterministic and probabilistic classification for compliance assessment against an upper limit. Adapted from [6].

Sampling uncertainty is defined as the part of the total measurement uncertainty attributable to sampling [3,8]. Principles and procedures for estimating the uncertainty of measurement arising from sampling are described in the Guide published by Eurachem and CITAC [11] as well as in the Nordtest handbook [8] which is intended for practical applications.

There are two broad approaches for the estimation of uncertainty, the modeling method and the empirical method [12,13,10]. The modeling approach which is consistent with ISO GUM [14] and is described as a "bottom up" approach [15], quantifies all sources of uncertainty individually, and then combines (propagates) them through a mathematical model. The implementation of the modeling approach reveals difficulties in establishing reliable estimates for the input variables of the model [12]. On the other hand the empirical approach, which is described as "top down" approach [15], uses replicated measurements in order to obtain a reliable estimate of the uncertainty, without necessarily knowing any of the sources individually [11–13]. One of the most commonly used empirical methods is the duplicate method with a balanced experimental design. This method involves the formation of duplicate samples from the sampling targets by applying the same sampling protocol and duplicate analysis of samples under repeatability conditions. Appropriate statistical analysis applied to the resulting data leads to the estimation of the sampling uncertainty.

The aim of this work is to present and compare three statistical approaches used for the estimation of the uncertainty caused by manual sampling of fuels from petroleum retail stations, utilizing the duplicate sampling method. Duplicate samples of automotive diesel from 104 petroleum retail stations (10.9% of the petroleum retail stations monitored for fuel quality purposes) were analyzed in duplicate for the determination of sulfur content according to ASTM D 5453 [16]. The sulfur mass content is one of the most critical parameters associated with automotive diesel specifications. The results of the measurements of the samples were analyzed using three statistical approaches, classical ANOVA, robust ANOVA and range statistics [8,17] and the sampling uncertainty under each approach was calculated. Sampling (and analytical) bias has been assumed to be zero in this study.

2. Sampling protocol and experimental design

A balanced nested experimental design was used. Duplicate samples were taken from 104 petroleum retail stations, which were selected at random and comprised the 10.9% of the 950 petroleum retail stations monitored by the laboratory. The scheme of sampling is shown in Fig. 2. The duplicated samples were taken by repeating the same sampling protocol. The sampling protocol used was consistent with the standard method ASTM D 4057 [2] concerning the manual sampling of petroleum and petroleum products. Instructions were given to the samplers to introduce variations to the sampling process provided that they do not violate any requirement of the sampling protocol. These variations actually represent variations which may arise due to the random nature of the sampling process. All automotive diesel samples were maintained in special closed containers. During transport and storage samples were protected to prevent weathering or degradation from light, heat or other potential detrimental condition.

3. Analytical method

The determination of sulfur mass content of diesel fuel samples was carried out in the Laboratory of Fuels and Lubricants Technology (National Technical University of Athens), which is operating under ISO 9001 [18] and ISO/IEC 17025 [19] management systems and participates successfully in Proficiency Testing Schemes for a range of fuel quality parameters (sulfur mass content included). The duplicated samples were analyzed in duplicate under repeatability conditions for sulful mass content determination. An ANTEK 9000S sulfur analyzer equipped with an automatic sampler was employed in this work. This analyzer fully complies with ASTM D 5453 [16] and ISO 20846 [20]. Table 1 presents the operating conditions of the instrument. The sample sulfur content in nanograms per microlitre ($ng\,\mu L^{-1}$) was

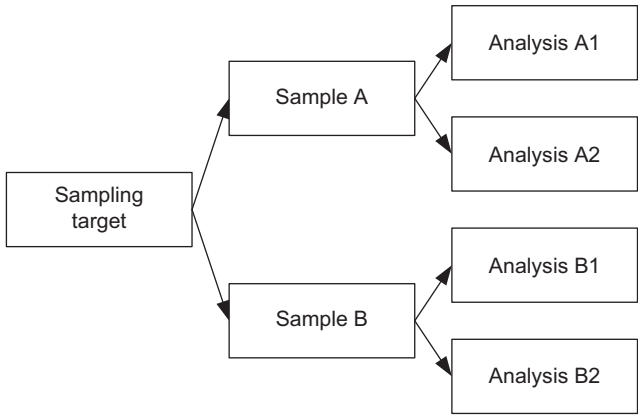

Fig. 2. Balanced experimental design employed for the estimation of sampling uncertainty.

Table 1
Instrument parameters used for total sulfur determination in petroleum products.

Parameter	Value
Volume injected (μL)	10
Syringe drive rate ($\mu L\,s^{-1}$)	1
Furnace temperature (°C)	1080
Furnace oxygen flowmeter setting ($mL\,min^{-1}$)	470
Inlet oxygen flowmeter setting ($mL\,min^{-1}$)	15
Inlet carrier (Argon) flowmeter setting ($mL\,min^{-1}$)	150