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ScienceDirect

Chemometrics and Intelligent Laboratory Systems 92 (2008) 3–12

Chemometrics and intelligent laboratory systems

www.elsevier.com/locate/chemolab

Measurement uncertainty in the determination of total petroleum hydrocarbons (TPH) in soil by GC-FID

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Received 28 June 2007; received in revised form 24 October 2007; accepted 24 November 2007
Available online 4 December 2007

Abstract

In this investigation two methods were used for estimating the measurement uncertainty due to sampling and analysis of petroleum hydrocarbon contaminated soil. Analysis of variance (ANOVA) was used for type A evaluation of the measurement uncertainty. The results showed that the statistical evaluation of measurement uncertainty can be complicated by the log-normality and heteroscedasticity of the data. Although mathematical transformation of raw data is widely suggested for overcoming the discrepancy between data and ANOVA assumptions, its use results in problems with the interpretation of the ANOVA results at the original scale.

The measurement uncertainty was also estimated from the calculated precision equations for sampling and analysis. Comparison of measurement uncertainty values with the equivalent values obtained with ANOVA revealed that ANOVA overestimates the expanded uncertainty at both low and high TPH concentrations. Consequently, correct selection of the statistical analysis method needs comprehensive knowledge of the assumptions and limitations of statistical methods and careful consideration of the special characteristics (distribution, constancy of measurement variance) of the raw data as these may affect the validity of the estimated uncertainty. The expanded uncertainty obtained in this study for the results of TPH determinations with linear measurement precision modelling was moderate, ranging from 21% at a TPH concentration of 895 mg/kg to 9% at a TPH concentration of 10 019 mg/kg. If a single sample taken in a survey is analyzed only once, then the analytical variance contributes the most to the measurement variance, ranging from 68– 80% at a TPH concentration of 100–10 000 mg/kg.

Keywords: Total petroleum hydrocarbons; Analytical uncertainty; Sampling uncertainty; Analysis of variance; Precision; Contaminated soil

1. Introduction

General rules for evaluating and expressing uncertainty in measurements were established by ISO in 1993 [1]. The aim was to unify the method used for evaluating and expressing uncertainty and, consequently, to bring coherence to all scientific measurements. The implications of these general rules for environmental protection were realised in the late 1990's. The research done at the time indicated that the use of measurement uncertainty in the interpretation of environmental monitoring results could reduce the risk of misinterpretations and, consequently, reduce the chance of underestimating the risks to human health or the environment. The concept of measurement uncertainty was also found to have significant implications for environmental risk assessment, for the identification of causes of measurement uncertainty, and for the remediation costs of contaminated areas. Therefore, as confidence in analytical data has been shown to be a prerequisite for meeting the objective of correct decision-making, the estimation of measurement uncertainty is now accepted as an essential national objective in the development of the environmental monitoring of harmful substances [2].

According to the internationally accepted approach [1], the reliability of measurement data can be expressed by stating the expanded uncertainty of a measurement result. When applied to environmental analytics, this approach implies that both the primary sampling and analytical stages must be recognized as sources of uncertainty [3,4]. The concept of analytical uncertainty has been recognized by analytical chemists for a long time. EURACHEM/CITAC has introduced documents showing how the concepts of ISO should be applied in chemical measurements

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doi:10.1016/j.chemolab.2007.11.006

[5], and how the procedures needed for the uncertainty estimation process should be integrated with existing quality assurance measures in analytical chemistry [6]. However, the quality assurance of primary sampling process is not as well developed. In actual fact, the uncertainty associated with sampling is not explicitly treated by EURACHEM/CITAC, either. Nevertheless, it has been shown that, especially in the case of geochemical investigations, the primary sampling stage usually contributes the largest source (50– 70%) of measurement uncertainty [3,7,8] and therefore its contribution should be included in the uncertainty estimate of environmental results. Only then can the geochemical interpretation of analytical results be made correctly.

The research carried out in the area of measurement uncertainty has presented few possibilities for estimating the uncertainties introduced by the analytical and field sampling stages [9–12]. One of such methodologies designed for geochemical surveys and quality control utilizes a balanced or unbalanced experimental design of replicated primary samples and analyses. The total variance of the results can then be broken down into three components by classical analysis of variance (ANOVA). One of these variance components represents the between-location variance due to the real variation of the analyte across the sampling target (s^2_{geo}). The other two variance components, which arise from the primary sampling (s^2_{sampl}) and analysis (s^2_{anal}) stages, can be combined to give the estimate of measurement variance (s^2_{meas}) [7]. If the presence of analytical bias can not be demonstrated, then the expanded uncertainty U_{meas} can be calculated as $U_{meas} = k \cdot s_{meas}$, where $k = 2$ for 95.5% confidence.

As a parametric statistical method, however, classical ANOVA relies on the assumptions of normality of the distribution and of homoscedasticity of the variances. These conditions are, however, rarely met in the case of environmental contaminants. A number of studies have shown that the distribution of contaminants in the environment often display log-normal distributions [13]. Also, the range of analyte concentrations in a study area will not necessarily be narrow, and therefore it is reasonable to assume that a change in measurement precision can be expected within this concentration range. Significant autocorrelation of observations may also increase the risk that ANOVA will overestimate the extent of the difference between the variables. Utilization of classical ANOVA should therefore be preceded by thorough inspection of the data as violations of ANOVA assumptions may affect the power and significance level of the test and, consequently, result in reduced reliability of ANOVA estimations. However, the question still remains of whether the potential violations will significantly affect the feasibility of the ANOVA results.

Robust statistics can be used to reduce the problems with the assumptions of normality and homoscedasticity [12]. With robust ANOVA the outlying values are down-weighted rather than neglected, and the effect of heteroscedasticity is then assumed to decrease. Log-transformation of raw data has also been used for this purpose [13,14] because log-transformed values often closely fit the normal distribution. The log-transformation may also be carried out to stabilize the heteroscedasticity of the variances [15]. Classical ANOVA can then be used to analyze the log-transformed data. Back-transformation of ANOVA results, however, is needed as it is more feasible to present the obtained mean ($\bar{x}$) and its standard deviation (s) in terms of the original rather than the log-transformed scale. In this case the exponentiated mean ($e^{\bar{x}}$) will represent not the arithmetic mean but the geometric mean ($\bar{x}^*$) of the log-normal distribution [16]. Correspondingly, as the 95% confidence interval of the transformed mean ($\bar{x}$) is given by $\bar{x} \pm 2s$, then the confidence interval at the original scale is calculated as $\bar{x}^* \overset{\times}{\div} (s^*)^2$. Due to the asymmetry of the log-normal distribution, this confidence interval will be asymmetric about the sample geometric mean. This form of stated uncertainty will subsequently differ from the general guidelines given by EURACHEM/CITAC for reporting the expanded uncertainty of a chemical measurement.

According to recent results [17], transformation of raw data into a homoscedastic population is not needed because linear precision modelling methods can be used to estimate the measurement precision change with concentration. The theoretical grounds for the estimation of analytical precision using duplicate analysis was introduced by Thompson and Howarth [18,19]. The approach was further developed by Lee and Ramsey to model both the analytical uncertainty and the primary sampling uncertainty as a function of concentration [17]. Using this methodology, the measurement uncertainty for the range of analyte concentrations in question can then be calculated as a combination of the linear models of sampling and analysis.

As discussed in the above, there are few possibilities available for estimating sampling and analytical uncertainties. So far, this methodology has mainly been applied in estimating measurement uncertainty in the case of heavy metal determination. However, the methodology will be as equally applicable to the estimation of measurement uncertainty in the case of organic contaminants. In this investigation, two different methods were used to estimate the measurement uncertainty for the determination of total petroleum hydrocarbons (TPH) in soil. Emphasis was put on comparing the measurement uncertainty values obtained. The aim was to indicate that, although a number of methods are available for evaluating measurement uncertainty, selection of the most applicable method requires a comprehensive knowledge of the limitations of statistical methods and careful consideration of the special characteristics (distribution, constancy of measurement variance) of the measurement data as these may affect the validity of the estimated uncertainty. Otherwise the expanded uncertainty becomes uncertain itself, and no advantage is gained to support the end-use of the data.

2. Materials and methods

2.1. Case study area

The case study area which has been used for the retail sale of petroleum products is located in South Ostrobothnia, Finland. On the basis of risk assessment the site was accepted in the national remediation program (SOILI programme) implemented by the Finnish Gas and Petroleum Federation. The investigated