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Article

# Uncertainty Estimation Related to Analysis of Volatile Aromatic Hydrocarbons by Static Headspace Gas Chromatography

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**A study of the analysis of benzene, toluene, ethylbenzene and xylenes by static headspace gas chromatography illustrated the estimation of uncertainty associated with the influence of several parameters, such as preparation of the standard solutions, calibration of the instrument, recovery and limit of detection. The objective of the investigation was to indicate the contribution of each stage in the developed procedure on the uncertainty measurement of the determination of volatile aromatic hydrocarbons in surface and underground water. The uncertainty sources were identified and illustrated in an effect diagram. The data illustrated the evaluation of uncertainty by the quantification of the uncertainty arising separately from each source. It has been demonstrated that data can be used to estimate the uncertainty resulting from the combined effect of all sources.**

## Introduction

The estimation of uncertainty is a general method of quality assurance in a laboratory (1). According to EN ISO/CEI 17025:2006, all certified laboratories must possess and apply procedures to estimate the uncertainty of the measurements (2). The estimation of measurement uncertainty, together with the development of a method and the determination of the other key parameters of performance, is an important step in the procedure of validating a quantitative method (3–7). According to the definition, the uncertainty of measurement is a parameter associated with the result of the measurement and characterizes the dispersion of values that can reasonably be attributed to the measurand. Over the past few years, substantial efforts have been made to improve the methodology for estimating analytical uncertainty. The concepts and practices of analytical uncertainty assessment are well documented and are recognized by analytical chemists. Eurachem/CITAC has published documents showing how the concepts of the International Standards Organization (ISO) Guide should be applied in chemical measurements, and how the procedures needed for the process of uncertainty estimation should be integrated with existing quality assurance measures in analytical chemistry (8). Several examples of uncertainty evaluations can be found in the Eurachem/CITAC Guide with relevance to acid/base titration, chromatography, atomic absorption spectrometry, double isotope dilution and inductively coupled plasma mass spectrometry (3). This guide illustrates the validation of a method for the determination of pesticides in food, employing liquid extraction and gas chromatography (GC) procedures that can be used to estimate uncertainty. The validation data are proposed as a valuable source of input for the calculation of uncertainty, but no principle is proposed for a systematic use of this information.

There are still difficulties with the determination of measurement uncertainties, and this study attempts to show how this task can be achieved. When estimating the uncertainty of measurement, all uncertainty sources that are of importance in the given situation are taken into account using the accepted method of analysis. This work assessed the contribution of each step of the developed method on the uncertainty of the measured results connected with the determination of volatile aromatic hydrocarbons in surface and underground water by using GC with flame ionization detection (FID). A headspace method was employed for isolation and preconcentration of the volatile aromatic hydrocarbons from samples.

## Experimental

### *Chemicals and reagents*

The experimental investigations based on a certified combination of reference and organic material (Mix 8240-24), consisting of benzene, toluene, ethylbenzene and xylenes (BTEX) in methanol (final concentration for each compound was 2,000 µg/mL ± 0.6%; Lot C1100319001), which was manufactured by SPEX CertiPrep Group (SPEX CertiPrep Inc., Metuchen, NJ). The HPLC-grade methanol (99.9%) and Uvasol acetone for spectroscopy (99.9%) were purchased from Merck (Darmstadt, Germany). By diluting the stock solution (2,000 µg/mL) with ultrapure water, working calibration solutions of 2.0, 20 and 100 µg/mL were prepared in the laboratory. Dilutions were performed with class A volumetric glassware. All calibration solutions were equilibrated at 20°C before preparation and use.

Aquacheck proficiency testing sample 18C (BTEX) was obtained from LGC Standards Proficiency Testing (Middlesex, UK).

### *Apparatus*

Headspace analysis was performed by using a Hewlett-Packard 7694 headspace sampler. Experimental optimum parameters of the headspace sampler were as follows: vial equilibration time, 60 min; extraction temperature, 95°C; sample loop volume, 3 mL; loop temperature, 120°C; transfer line temperature, 150°C; loop fill time, 0.30 min; injection time, 1.0 min; sample volume, 10 mL.

A Hewlett-Packard model 5890 Series II GC equipped with an FID system was used for the final BTEX determinations.

The GC column was an HP-1 fused silica capillary column, 30 m in length × 0.53 mm id × 2.65 µm film thickness. The carrier gas was helium at 10 mL/min; the injector and detector port temperatures were 200 and 250°C, respectively. The CG separation was performed under the following conditions: column temperature programmed from 35°C (3 min) to 65°C (0 min) at a rate of 4°C/min, followed by a rate of 12°C/min to 190°C and held for 10 min.

## Results

One of the most critical areas in water analysis is the isolation and preconcentration of the volatile aromatic hydrocarbons from samples. This is the most labor-intensive step and the source of many errors. The compounds of interest must be separated from the matrix. Many parameters have been optimized for the successful analysis of BTEX. A chromatogram is shown in Figure 1. As shown in the figure, the peaks of BTEX are symmetrical and separation of the analytes from the background components in the water samples is good.

The linear range of the FID was determined before BTEX analysis. The detector response was established for BTEX. The linearity of BTEX was obtained from sample preparation in ultrapure water as a blank matrix and was studied by evaluating the calibration curve at three concentrations levels: 2.0, 20 and 100 μg/mL. The calibration curves serve as a graphical representation of the measured signal as a function of the quantity of analytes. The calibration curve was examined by computing a regression line of the peak area for BTEX to the concentrations by using the least-squares fit; the linear relationship was demonstrated with correlation coefficients greater than 0.995. A multiple-point calibration was performed with the following linear regression mode:

$$y = a + bCi \quad (1)$$

where $y$ represents the response of the measurement system for the analyte concentration, $Ci$ (μg/mL); $a$ is the intercept of the curve; $b$ is the slope of the curve.

The three calibration standards were measured five times each, providing the mean values of the different calibration standards, slopes and intercepts for each aromatic hydrocarbon.

The precision, calculated as relative standard deviation (RSD), was less than 6%. The accuracy, as bias, was measured by spiking the sample with a known concentration (10 μg/mL) of each aromatic hydrocarbon; it was generally less than 9%. The sensitivity for all compounds was high and the limits of detection (LDs) varied between 0.8 and 1.6 μg/L. The LDs were calculated by using the standard deviation (SD) of 10 replicates at 1 μg/L for BTEX.

## Discussion

The estimation of uncertainty has become an integral part of quantitative method analysis. The global uncertainty of the method developed for the determination of BTEX in water was given by the uncertainty attributable to the processing of the sample and the uncertainty associated with plotting the calibration graph. The developed headspace GC method includes several working steps, such as pipetting and dilution, followed by injection, separation on a capillary column, detection and data processing (integration). These procedures were needed for both water sample analysis and reference material calibration.

The Ishikawa diagram was applied to evaluate the uncertainty of the method. Drawing a diagram clearly showed the understanding of the prepositional approach for uncertainty measuring. This diagram shows all factors that influence the end result of the analytical process (Figure 2). Each factor was represented through a side branch of the primary arrow. The diagram contains the influence of parameters such as accuracy of glassware (pipettes and flasks); maximum permissible error of glassware; accuracy of balance; SD of balance; purity of compounds, calibration of instrument; recovery ($R$); LD. Subsequently, this was used for establishing the budget of uncertainty for the proposed method. The Ishikawa diagram was used to calculate the uncertainty ($u$) of the final result and increased the understanding of how an analytical method works.

The uncertainty associated with the volumetric glassware (measuring cylinders, pipettes, flasks and headspace vials) was related to the calibration volume of the glasswork, the

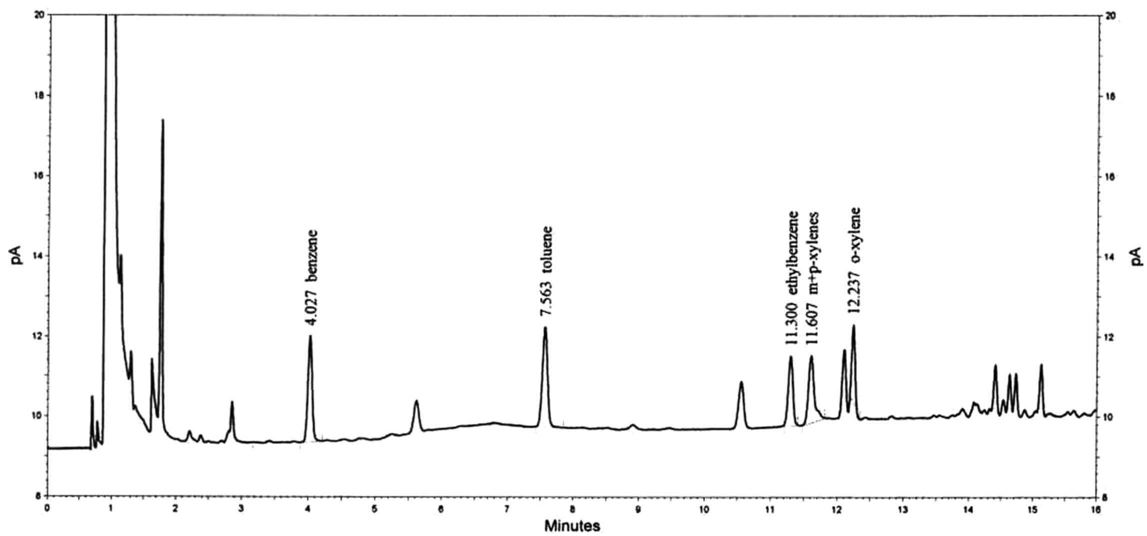


**Figure 1.** Chromatogram of BTEX in a surface water sample.

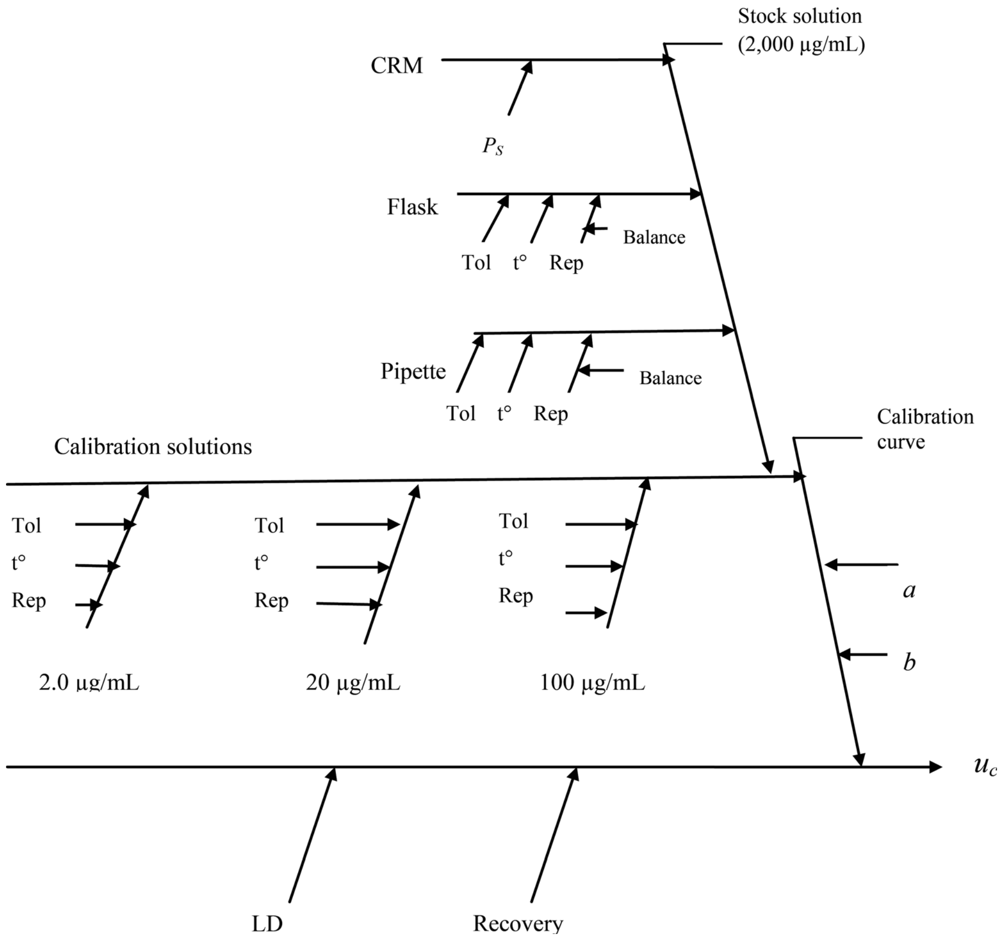


**Figure 2.** Ishikawa diagram for the determination of BTEX in surface and underground water.

repeatability of filling the glassware and the differences in temperature between the calibration and the laboratory room. The manufacturer specified that the nominal volume of glasswork should be measured at a temperature of 20°C without a level of confidence. In this situation, standard uncertainty of the volumetric glassware was treated as a rectangular distribution, which was calculated by dividing the tolerance (mL) by $\sqrt{3}$. The uncertainty of repeatability of filling the glassware was determined by applying a test filling ($n = 10$) of a 10 mL flask with water and weighing the volume. The SD from 10 measurements was measured as the standard uncertainty of repeatability of the filling. The glassware were calibrated at a temperature of 20°C and the laboratory temperature was maintained at $20 \pm 5$°C. The uncertainty attributable to the effect on the volume of water was taken into account by using the volume expansion coefficient for water, the difference between working laboratory temperature and calibration temperature of glassware, and measured volume. The standard uncertainty associated with volumetric glassware was calculated by assuming a rectangular distribution. Table I presents data for the contribution of standard uncertainties in the construction of the combined standard uncertainty of the volumes used in the development of the method.

The uncertainty associated with the analyte used for the preparation of standard solutions was related to the purity of the reference material and its mass (quantity). The purity of the aromatic compounds was given on the certificate for the reference material as $y$ (%). The purity was potentially an additional uncertainty source, with standard uncertainty of $(100 - y)/2\sqrt{3}$ (rectangular distribution). However, the contribution of this uncertainty was so small that it was neglected in the evaluation of this source of uncertainty (example in Table II). The uncertainty derived from the volume measurement and mass of the analyte was combined to obtain the standard uncertainty in the preparation of calibration solutions of the analyte to calibrate the instrument. Kragten's method was followed to calculate the standard and combined standard uncertainties of all calibration

**Table I**
Combined Standard Uncertainty of the Volumetric Glassware Used for the Method

| Volume (mL) | Standard uncertainty (mL) | | | Combined standard uncertainty (mL) |
|---|---|---|---|---|
| | Temperature influence | Repeatability | Calibration | |
| 0.5 | 0.0006 | 0.000125 | 0.00289 | 0.00295 |
| 1 | 0.0012 | 0.00025 | 0.00404 | 0.0042 |
| 5 | 0.006 | 0.00125 | 0.01732 | 0.0184 |
| 10 | 0.012 | 0.0025 | 0.02887 | 0.0314 |
| 100 | 0.05 | 0.025 | 0.04 | 0.069 |

**Table II**
Kragten's Diagram Used for the Calculation of Uncertainty Associated with the Preparation of a 2 μg/mL Concentration Level

| Number | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| 1 | | | m (μg) | $V_1$ (mL) | $V_2$ (mL) | $V_3$ (mL) | $V_4$ (mL) |
| 2 | | Value | 2000 | 1.0 | 10 | 1 | 100 |
| 3 | | Combined uncertainty | 0.059 | 0.0042 | 0.0314 | 0.0042 | 0.069 |
| 4 | m (μg) | 2,000 | 2,000.059 | 2,000 | 2,000 | 2,000 | 2,000 |
| 5 | $V_1$ (mL) | 1 | 1 | 1.0042 | 1 | 1 | 1 |
| 6 | $V_2$ (mL) | 10 | 10 | 10 | 10.0314 | 10 | 10 |
| 7 | $V_3$ (mL) | 1 | 1 | 1 | 1 | 1.0042 | 1 |
| 8 | $V_4$ (mL) | 100 | 100 | 100 | 100 | 100 | 100.069 |
| 9 | | | | | | | |
| 10 | $C_0$ (μg/mL)* | 2.0 | 2.000059 | 2.0084 | 1.9937 | 2.0084 | 1.9986 |
| 11 | $u(y, x_i)$† | | −0.000059 | 0.0084 | 0.0063 | −0.0084 | 0.0014 |
| 12 | $u(y)^2$, $u(y, x_i)^2$‡ | 0.00018 | 3.55E−9 | 7.0E−05 | 4.0−05 | 7.0E−05 | 2.0E−6 |
| 13 | $u(prep)$§ | 0.013 | | | | | |

*$C_0 = m \times V_1 \times V_3/V_2 \times V_4$.
†Differences of C10−G10 values minus value of B10.
‡Values of cells C11−G11 were squared and summed to provide the value in cell B12.
§Combined standard uncertainty.

**Table III**
Combined Standard Uncertainty Associated with the Preparation of Calibration Solutions

| Analyte | Concentration level, $C_0$ (μg/mL) | Standard uncertainty (μg/mL) | Combined standard uncertainty, $u(prep)$ (μg/mL) |
|---|---|---|---|
| Calibration solutions of BTEX | 2.0 | 0.00018 | 0.013 |
| | 20 | 0.03 | 0.17 |
| | 100 | 0.8 | 0.9 |

**Table IV**
Parameters of Calibration Curves

| Analyte | Parameters of calibration curves | | | | | |
|---|---|---|---|---|---|---|
| | $a$ (intercept) | SD of intercept | $b$ (slope of curve) | SD of slope of curve | $S_0$ | $r^2$ |
| Benzene | 236.8 | 37.5 | 142.1 | 0.3 | 112.1 | 0.999 |
| Toluene | 695.1 | 31.7 | 138.7 | 0.3 | 94.9 | 0.999 |
| Ethylbenzene | 331.1 | 41.6 | 113.4 | 0.3 | 124.5 | 0.996 |
| m- + p-Xylene | 1,027.3 | 444.3 | 102.6 | 1.9 | 1,330.9 | 0.995 |
| o-Xylene | 440.2 | 99.4 | 155.0 | 0.8 | 297.9 | 0.999 |

**Table V**
Standard Uncertainty, $u(cal)$, Associated with Plotting the Calibration Curves

| $C_0$ (μg/mL) | Benzene | | Toluene | | Ethylbenzene | | m- + p-Xylene | | o-Xylene | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $u(cal)$ (μg/mL) | RSD (%) | $u(cal)$ (μg/mL) | RSD (%) | $u(cal)$ (μg/mL) | RSD (%) | $u(cal)$ (μg/mL) | RSD (%) | $u(cal)$ (μg/mL) | RSD (%) |
| 2.0 | 0.03 | 1.5 | 0.02 | 0.9 | 0.03 | 1.4 | 0.05 | 2.4 | 0.03 | 1.5 |
| 20 | 0.3 | 1.5 | 0.4 | 2.0 | 0.2 | 1.0 | 0.5 | 2.5 | 0.2 | 1.0 |
| 100 | 3 | 3.1 | 2.5 | 2.5 | 2.2 | 2.1 | 2.6 | 2.5 | 1.5 | 1.5 |

**Table VI**
Standard Uncertainty Associated with Recovery and LD

| Aromatic hydrocarbons | Recovery (%) ($n$ = 5) | SD (%) | $u(R)$ (%) | LD (μg/L) ($n$ = 10) | SD (μg/L) | $u(LD)$ (μg/L) |
|---|---|---|---|---|---|---|
| Benzene | 90.7 | 1.5 | 0.67 | 0.9 | 0.097 | 0.03 |
| Toluene | 91.2 | 2.3 | 1.03 | 1.0 | 0.10 | 0.03 |
| Ethylbenzene | 95.0 | 1.9 | 0.85 | 1.2 | 0.15 | 0.05 |
| p-Xylene | 95.8 | 3.6 | 1.61 | 1.6 | 0.16 | 0.05 |
| o-Xylene | 93.4 | 2.6 | 1.16 | 0.8 | 0.085 | 0.03 |

**Table VII**
Standard Uncertainty and Expanded Uncertainty

| Aromatic hydrocarbons | Standard uncertainty ($u_c$) (μg/mL) | | | Expanded uncertainty ($U$) (μg/mL) | | |
|---|---|---|---|---|---|---|
| | 2.0 μg/mL | 20 μg/mL | 100 μg/mL | 2.0 μg/mL | 20 μg/mL | 100 μg/mL |
| Benzene | 0.07 | 0.8 | 4 | 0.1 | 1.6 | 8 |
| Toluene | 0.07 | 0.8 | 4 | 0.1 | 1.6 | 8 |
| Ethylbenzene | 0.09 | 0.9 | 5 | 0.2 | 1.8 | 10 |
| p- + m-Xylene | 0.09 | 0.9 | 5 | 0.2 | 1.8 | 10 |
| o-Xylene | 0.08 | 0.8 | 4 | 0.2 | 1.6 | 8 |

solutions at different concentration levels of aromatic hydrocarbons (3). The resulting uncertainty in preparing the calibration solution at a concentration level of 2.0 μg/mL is reported in Table II. The combined standard uncertainty, $u(prep)$, associated with the preparation of the calibration solutions used for method development is indicated in Table III.

The results of plotting the calibration curves for each compound were used to calculate uncertainty associated with the instrument calibration. The parameters of the calibration curves are presented in Table IV. The uncertainty associated with the linear calibration curve of each aromatic hydrocarbon was given as follows:

$$u(cal) = \frac{S_0}{b}\sqrt{\frac{1}{p} + \frac{1}{n} + \frac{\left(Y_j - Y_{av}\right)^2}{b^2 \sum_{j=1}^{n} \left(C_j - C_{av}\right)^2}} \qquad (2)$$

where $S_0$ is the residual standard deviation of linear regression model; $b$ is the slope of curve; $p$ is the number of measurements to determine $C_j$; $n$ is the number of solutions for plotting the calibration curve; $Y$ is the measured area of aromatic hydrocarbon; $C$ is the aromatic hydrocarbon concentration (μg/mL); $j$ is the index for the number of measurements to obtain calibration curve; $av$ is the index for the average value.

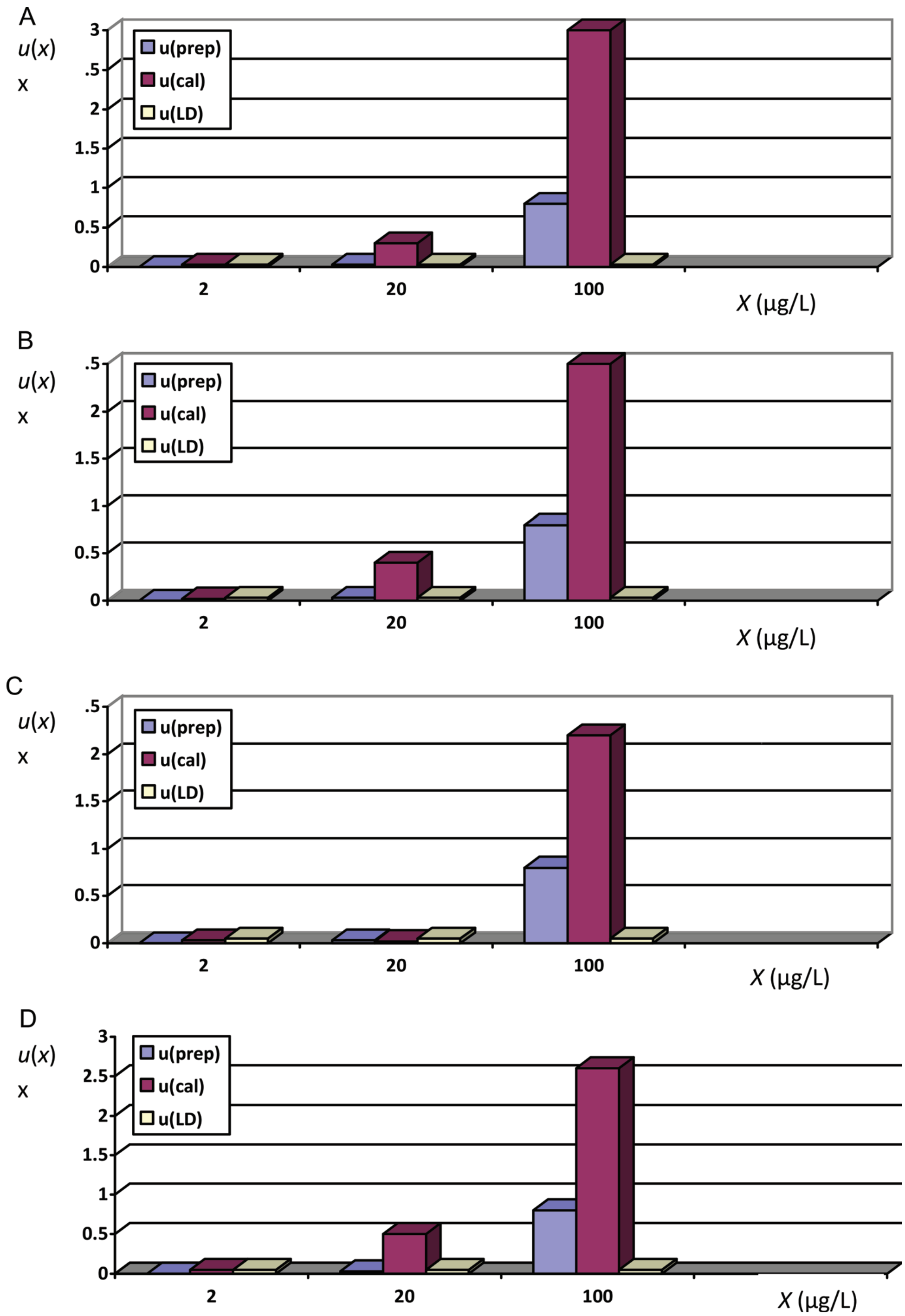


**Figure 3.** Uncertainty contributions for the determination of BTEX in water samples: benzene (A); toluene (B); ethylbenzene (C); p-xylene (D).

The obtained data from uncertainty calculation, $u(cal)$, associated with the calibration curve of each aromatic hydrocarbon are presented in Table V.

The recovery was determined from 90 to 96% for all tested compounds (Table VI). The uncertainty associated with recovery was calculated from values obtained from the average recovery in concentration range of 2.0–100 μg/mL. The standard uncertainty was calculated as the SD of the mean recovery divided by the square root of the number of recovery results ($n = 5$). A Student's $t$-test was used to determine whether the mean recovery was significantly different from 1.0, because recovery of 100% was accepted for reference. The statistical test was calculated by using the following equation:

$$t = \frac{|1 - R|}{u(R)} \tag{3}$$

The values were compared with those in the table for $n - 1$ degrees of freedom at 95% confidence (where $n$ is the number of results used for the estimation of $R$) (9). If the calculated $t$ value is greater than in the table, then $R$ is significantly different than 1.0.

The standard uncertainty associated with the LD was calculated as the SD of the mean LD of each aromatic hydrocarbon divided by the square root of the number of results ($n = 10$). The uncertainty in determining the detection limit was varied between 0.03 and 0.05 µg/L.

The combined standard uncertainty was given by the following expression:

$$\frac{u_c}{C_0} = \sqrt{\left(\frac{u(prep)}{C_0}\right)^2 + \left(\frac{u(cal)}{C_0}\right)^2 + \left(\frac{u(R)}{R}\right)^2 + \left(\frac{u(LD)}{LD}\right)^2} \quad (4)$$

where $u_c$ is the combined standard uncertainty (µg/mL); $C_0$ is the concentration level (µg/mL); $R$ is the recovery (%); $LD$ is the limit of detection (µg/L); $u(prep)$ is the uncertainty associated with preparation of the calibration solutions (µg/mL); $u(cal)$ is the uncertainty associated with the plotting the calibration curves (µg/mL); $u(R)$ is the uncertainty associated with the recovery; $u(LD)$ is the uncertainty associated with the LD.

The values of measurement uncertainty were expressed in terms of expanded uncertainty ($U$), which was determined by multiplying the combined standard uncertainty, $u_c$, with a coverage factor $k = 2$; for normal distribution, this provides a level of confidence of approximately 95%. The obtained values of $u_c$ and $U$ for each aromatic hydrocarbon and different concentration levels are presented in Table VII.

On the basis of the Ishikawa diagram and all calculations connected with this diagram, the conclusion can be drawn that from the uncertainty of the analytical procedure, the largest influence is the uncertainty connected with the plotting the calibration curves. In this respect, Figure 3 shows that all of the sources of uncertainty were adequately determined.

Uncertainty measurement allows a result to be evaluated and compared with other results, especially those from other laboratories (10). It is very important to determine that the method is capable of satisfying some requirements within the expected range of precision. The developed method was evaluated by using certified Aquacheck proficiency testing sample 18C (BTEX). The standard uncertainty of the median reference values was estimated with the standard uncertainty of the obtained values. These comparisons were shown in Table VIII. The results of participation were satisfactorily assessed by the presented $z$-scores, which are: 0.35 (benzene), 1.21 (toluene), 1.41 (ethylbenzene), −0.03 (p + m-xylene), 0.95 (o-xylene). The $z$-score is a measure of the difference between the reported concentration and the reference value. An absolute $z$-score of $|z| \leq 2$ indicates a satisfactory result. It was concluded that analytical method was appropriate, sensitive and provides a global estimation of the uncertainty. The positive meaning of measurement uncertainty was communicated to the superiors of this laboratory and to the customers.

**Table VIII**
Results of an Interlaboratory Test of Sample 18C

| Aromatic hydrocarbons | Lab | Median reference value (µg/L) | $u_c$ (µg/L) | Robust RSD (%) | Obtained value (µg/L) | $u_c$ Lab (µg/L) | $z$-Score |
|---|---|---|---|---|---|---|---|
| Benzene | 34 | 12.7 | 2.1 | 12.5 | 13.2 | 0.4 | 0.35 |
| Toluene | 36 | 49.4 | 2.4 | 14.7 | 55.4 | 0.5 | 1.21 |
| Ethylbenzene | 33 | 29.9 | 2.5 | 14.2 | 34.1 | 0.3 | 1.41 |
| p- + m-Xylene | 21 | 57.1 | 2.4 | 10.9 | 56.9 | 0.6 | −0.03 |
| o-Xylene | 34 | 21.9 | 2.0 | 11.2 | 24.8 | 0.4 | 0.95 |

## Conclusion

Four sources of uncertainty were taken into consideration in this study. These included the uncertainties associated with the preparation of the calibration solution, the plotting of calibration curves, recovery and LDs. The Ishikawa diagram is very simple, which is why it was used to calculate the uncertainty. The estimation of the uncertainty components showed that it was a suitable tool for the experimental design to obtain the uncertainties in the analytical result. The uncertainty associated with the calibration of the GC appears to be the most important source in the overall uncertainty, which requires analysts to pay great attention when conducting calibrations of instrumental techniques.

In this study, the highest extended uncertainty was associated with the determination of ethylbenzene and m- and p-xylene. The uncertainty values correlated with the higher SDs of the slopes of calibration curve obtained for these compounds. The uncertainty in determining the detection limit varied from 3% (toluene) to 4.2% (ethylbenzene). The uncertainty of recovery was quite low: 0.7% (benzene) to 1.7% (p-xylene).

## References


1. Olivares, I.R.B., Lopes, F.A.; Essential steps to providing reliable results using the analytical quality assurance cycle; *Trends in Analytical Chemistry*, (2012); 35: 109–121.
2. EN ISO/IEC 17025:2006. General requirements for the competence of testing and calibration laboratories. CEN/CEN-ELEC, Brussels, Belgium.
3. Ellison, S.L.R., Williams, A. (eds); Eurachem/CITAC guide: Quantifying uncertainty in analytical measurement, 3rd edition, (2012). www.eurachem.org.
4. Meyer, V.R.; Measurement uncertainty; *Journal of Chromatography A*, (2007); 1158: 15–24.
5. Nordtest Technical Report 537, Handbook for calculation of measurement uncertainty in environmental laboratories. Nordtest, (2003). www.nordtes.org.
6. Konieczka, P., Namieśnik, J.; Estimating uncertainty in analytical procedures based on chromatographic techniques; *Journal of Chromatography A*, (2010); 1217: 882–891.
7. Armishaw, P.; Estimating measurement uncertainty in an afternoon. A case study in the practical application of measurement uncertainty; *Accreditation and Quality Assurance*, (2003); 8: 218–224.
8. Guide to the expression of uncertainty in measurement, 1st edition. International Organization for Standardization, Geneva, Switzerland, (1993).
9. Taylor, J.K.; Statistical techniques for data analysis. Lewis Publisher, Inc., Chelsea, MI, (1990), pp. 65–85.
10. Ellison, S.L.R., Thompson, M., Westwood, D., Wood, R.; The role of proficiency testing in method validation; *Accreditation and Quality Assurance*, (2010); 15: 73–79.