

EVALUATION OF MEASUREMENT UNCERTAINTY IN THE DETERMINATION OF TOTAL PHOSPHORUS USING STANDARDIZED SPECTROMETRIC METHOD ISO 6878

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Abstract

The measurement uncertainty of the result of total phosphorus determinations in wastewater was evaluated. Total phosphorus was determined spectrometrically using ammonium molybdate (ISO 6878, 1998). The major sources of uncertainty of the result of measurement were identified as contributions from the linear least squares calibration, repeatability, homogeneity of the sample, storage conditions, and recovery. Identification and evaluation of sources of uncertainty was followed by combined uncertainty calculations. The results show that the major source of uncertainty arose from the calibration curve, thus leading to the conclusion that calibration is the target operation for reducing the measurement uncertainty of this determination.

Introduction

The result of a measurement is only an estimate of the true value of the measurand, and therefore needs to be accompanied by an estimate of the uncertainty – the range of the stated results. Even after all systematic effects have been corrected for, there remains uncertainty due to both random effects and imperfect corrections of the results of systematic effects. The overall uncertainty estimate gives a quantitative assessment of the reliability of the result, and allows the user of the results to compare it with other results of a similar type in a meaningful manner.

Traditionally, measurement uncertainty was not quantified and reported along with measurement results. What was reported was a standard deviation obtained from repeated measurements on the same test sample. Such reporting of data did not assure comparability of results as many sources affecting the reliability of these results were not accounted for, e. g. calibration, environmental effects, etc. To improve the situation, reporting of measurement uncertainty along with the measurement result is required. The Eurachem guide for “Quantifying Uncertainty in Analytical Measurement”¹ which is based on the “Guide to the Expression of Uncertainty in Measurement” published by ISO², recommends uncertainty be estimated from its components and by using rules for

propagation of errors in order to combine them into total uncertainty. The uncertainty budget published in this paper is based on these guidelines.

Additional evidence of the use of this approach is needed in chemical analysis of water and wastewater. Measurement uncertainty evaluations of the result of measurement is one of the requirements of standard ISO/IEC 17025³ which must be fulfilled by laboratories in order to obtain accreditation for certain test methods. Measurement uncertainty also has implications for interpretation of analytical results in regulatory areas such as wastewater effluent monitoring and taxation of wastewater pollution in Slovenia. Total phosphorus is one of the parameters for industrial and municipal wastewater effluent quality estimation.

The purpose of this paper was to demonstrate a procedure for evaluation of the uncertainty of the results of total phosphorus obtained by a spectrometric method and to identify the steps in the analytical procedure that may be improved with the goal of reducing the overall measurement uncertainty of the result.

The uncertainty evaluation process

The process of evaluation of the uncertainty of total phosphorus determination was divided into the following steps: description of the method, specification of the measurand and identification of uncertainty sources, quantification of uncertainty components and calculation of combined and expanded uncertainty.

Description of the method

The total phosphorus concentration was determined spectrometrically according to standardized method ISO 6878:1998(E)⁴. Phosphorus analyses embody two general procedural steps: (a) conversion of the phosphorus to dissolved orthophosphate, and (b) colorimetric determination of dissolved orthophosphate. Polyphosphates and organophosphorus compounds are converted to molybdate-reactive orthophosphate using potassium peroxodisulfate. Orthophosphate ions are reacted with an acid solution containing molybdate and antimony ions to form an antimony phosphomolybdate complex. The complex is reduced with ascorbic acid to form a strongly coloured blue

molybdenum complex. The absorbance of this complex is measured to determine the concentration of orthophosphate present.

In brief, the steps of the method are as follows: The test sample is pipetted into a borosilicate flask. 4 ml of potassium peroxodisulfate solution ($c=50$ g/l) is added and the sample is autoclaved for 30 minutes at a temperature between 115°C and 120°C . After the solution has cooled, pH is adjusted to between 3 to 10 with sodium hydroxide solution or sulphuric acid and transferred to a 50 ml volumetric flask. In each flask, 1 ml ascorbic acid ($c=100$ g/l) and 2 ml of acid molybdate solution (13 g of ammonium heptamolybdate tetrahydrate is dissolved in 100 ml of deionised water; 0.35 g of antimony potassium tartrate hemihydrate is dissolved in 100 ml of deionised water; the molybdate and tartrate solutions are added to 300 ml of sulphuric acid with a concentration 9 mol/l) is added. The volume is made up to the mark with deionised water and mixed. The absorbency of the sample is measured in triplicate using a spectrometer (Perkin-Elmer, Lambda 20 UV/VIS) at 880 nm after 10 minutes.

The calibration curve is established by measuring a series of total phosphorus reference solutions (0.04 mg/l; 0.08 mg/l; 0.12 mg/l; 0.20 mg/l; 0.32 mg/l; 0.40 mg/l). A stock reference solution (C_p) with a concentration of 50 mg/l is prepared by drying potassium dihydrogen phosphate (Merck, Germany) to constant mass at 105°C , weighing the salt and dissolving it in a volumetric flask with deionised water (Millipore, France). Working reference solutions are prepared by further dilution. After preparation of the reference solutions, the procedure followed is the same as for samples. The absorbance of each reference solution is measured on six replicates. A new calibration curve is established every time new batches of chemicals are used. It is checked at two levels at the beginning of each run.

The blank signal is obtained by the same procedure, using the same quantities of reagents as in the determination but using deionised water instead of the sample. Blank solution absorbencies are subtracted from sample absorbencies.

The choice of the working range, calibration and characteristics of the method are determined according to standard ISO 8466-1⁵.

The method was kept under continuous statistical control. A control chart was created from the results obtained in the analysis of an RM (laboratory working reference

standard). In addition a CRM (QCP 042-2, Promochem, Germany) was analyzed and no significant discrepancy between our results and the certified value was found. The laboratory also participates in proficiency tests (AQUACHECK, WRc plc, UK) and good performance in this determination has been obtained.

Specification of the measurand and identification of the sources of uncertainty

The main sources of uncertainty in the measurements were identified as the linear least squares calibration, the overall repeatability of the experiment, homogeneity, storage conditions, and recovery. Repeatability contributions to uncertainty were combined into one contribution for the overall experiment and values were obtained from the method validation study. The uncertainty associated with digestion of the sample was assumed to be negligible. With these corrections the concentration of total phosphorus (P_{tot}) in a sample was expressed by the model:

$$P_{\text{tot}} = \frac{A - B_0}{B_1} \cdot F_{\text{dil}} \cdot F_{\text{rep}} \cdot F_{\text{h}} \cdot F_{\text{s}} \cdot F_{\text{r}} \quad \text{Eq. 1}$$

where A is the measured absorbance of the sample, B_1 is the slope of the linear least squares calibration curve, B_0 is the calculated blank, F_{dil} is the dilution factor of the sample, F_{rep} is the correction factor for repeatability, F_{h} is the correction factor for homogeneity, F_{s} is the correction factor for storage conditions and F_{r} is the correction factor for recovery.

The slope of the linear least squares calibration curve B_1 and calculated blank B_0 were calculated from the equations:

$$B_1 = \frac{\sum_{i=1}^n (C_{P-i} - \bar{C}_P) \cdot (A_i - \bar{A})}{\sum_{i=1}^n (C_{P-i} - \bar{C}_P)^2} \quad \text{Eq. 2}$$

$$B_0 = \bar{A} - B_1 \cdot \bar{C}_P \quad \text{Eq. 3}$$

$$\bar{A} = \frac{1}{n} \sum_{i=1}^n A_i \quad \text{Eq. 4}$$

$$\bar{C}_P = \frac{1}{n} \sum_{i=1}^n C_{P-i} \quad \text{Eq. 5}$$

where C_{P-i} is the concentration of the reference solution at the i^{th} level ($C_{P-1}, \dots, C_{P-i}, \dots, C_{P-n}$) and A_i is the absorbance of the i^{th} reference solution ($A_1, \dots, A_i, \dots, A_n$).

The sources of uncertainty in total phosphorus determination are schematically presented in Figure 1.

Quantification of the uncertainty components

In this step uncertainties arising from each of the identified sources were quantified. Uncertainty components of a measurement result were deduced from two basically different types of evaluation: in type A, evaluations were estimated from a series of repeated observations by calculating the standard deviation of the mean, and type B evaluations were estimated as standard deviations from data from other sources, for example from information in the calibration certificates, or estimated by the analyst based on experience or general knowledge. Before calculating combined uncertainty, type B uncertainties were expressed as one standard deviation. If there were no data on the distribution, it was estimated as normal, rectangular, or triangular and then converted to a normal distribution².

Uncertainty associated with linear least squares calibration

The amount of total phosphorus was calculated using a previously prepared calibration curve according to the linear least squares fitting procedure. The uncertainty of the calculated concentration obtained from the calibration curve is associated with the uncertainty of the calibration solution concentrations and the uncertainty of the measured absorbencies of the reference solutions. Working reference solutions were prepared from a stock reference solution by dilution.

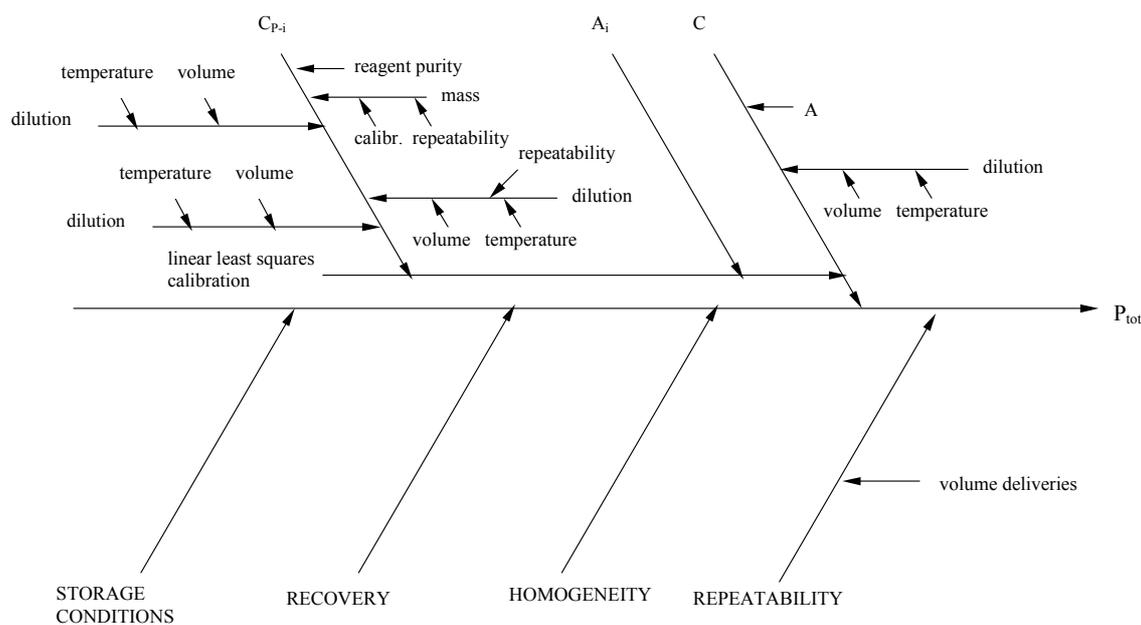


Figure 1 Cause and effects diagram for determination of total phosphorus using a spectrometric method

The concentration of the stock reference solution (C_P) was calculated as:

$$C_P = \frac{m_{\text{KH}_2\text{PO}_4} \cdot P_{\text{KH}_2\text{PO}_4} \cdot M_P / M_{\text{KH}_2\text{PO}_4}}{V_{1000}} \quad \text{Eq. 6}$$

where $m_{\text{KH}_2\text{PO}_4}$ is the mass of potassium dihydrogen phosphate, $P_{\text{KH}_2\text{PO}_4}$ is the purity of potassium dihydrogen phosphate, M_P is the atomic weight of phosphorus, $M_{\text{KH}_2\text{PO}_4}$ is the molar mass of potassium dihydrogen phosphate and V_{1000} is the volume of the volumetric flask for preparation of stock solution.

The uncertainty of the concentration of the stock calibration solutions is associated with the uncertainty of the mass of potassium dihydrogen phosphate, the purity of the reagent and the volume of the volumetric flask for preparation of stock solution. Uncertainties in the atomic weight of phosphorus and the molar mass of KH_2PO_4 were considered to be much lower in comparison with other uncertainties and were neglected.

The uncertainty associated with the reagent mass ($u(m_{\text{KH}_2\text{PO}_4})$) was obtained from the balance calibration certificate, while the uncertainty associated with the repeatability of weighing of the salt was obtained from successive weighing operations based on data from control charts. All the uncertainties were then combined according to the equation:

$$u(m_{\text{KH}_2\text{PO}_4}) = \sqrt{u(m_{\text{cal}})^2 + u(m_{\text{rep}})^2} \quad \text{Eq.7}$$

where $u(m_{\text{cal}})$ is the uncertainty of mass based on data from the balance calibration certificate and $u(m_{\text{rep}})$ is the repeatability of weighing.

The uncertainty associated with the volume of the volumetric flask depends on the uncertainty of volume of the volumetric flask itself, the uncertainty associated with the use of volumetric equipment at a temperature different from that of calibration and the repeatability of volume delivery for preparation of the reference stock solution (C_P). The limits of accuracy of the volumetric flask volume ($u(V_{\text{cal}})$) were indicated to be of type B uncertainty by the manufacturer with no data on distribution. The ISO guide recommends a triangular distribution assumption because values are expected to be more likely in the centre than near the bounds. Therefore to obtain the standard deviation, values were divided by $\sqrt{6}$. The second component corrects for errors associated with the use of calibrated volumetric equipment at temperatures different from those at which it was calibrated according to the manufacturer's instructions (20°C). The uncertainty of this effect, $u(V_T)$, was calculated from an estimate of the temperature range and the volume expansion coefficient. A temperature variation of $\pm 5^\circ\text{C}$ was taken as a reasonable estimate (with a 95% confidence). The volume expansion of water is considerably larger than that of glass, so only the former was considered. Our solutions can be treated as pure water because of their low concentrations. The

temperature variation of ΔT , and the volumetric expansion coefficient of water of $2.1 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ lead to a volume variation calculated as:

$$u(V_T) = \frac{V \cdot \Delta T \cdot 2.1 \times 10^{-4}}{1.96} \quad \text{Eq. 8}$$

The repeatability of volume delivery in preparation of stock reference solution was determined experimentally by a series of fill and weigh experiments on a volumetric flask.

All uncertainty contributions were then combined to obtain the uncertainty of the volume of the volumetric flask ($u(V_{1000})$):

$$u(V_{1000}) = \sqrt{u(V_{\text{cal}})^2 + u(V_T)^2 + u(V_{\text{rep}})^2} \quad \text{Eq. 9}$$

where $u(V_{\text{cal}})$ is the uncertainty associated with calibration of the volumetric flask obtained from the producer's certificate, $u(V_T)$ is the uncertainty associated with the use of volumetric equipment at temperatures different from that of calibration and $u(V_{\text{rep}})$ is the uncertainty of volume delivery in preparation of the stock reference solution.

The uncertainty associated with the purity of the reagent was calculated from the producer's specification. The purity of potassium hydrogen phosphate was given on the certificate and the value was divided by $\sqrt{3}$ to obtain the standard uncertainty (a rectangular distribution was assumed).

The uncertainty of the stock reference solution concentration was calculated as:

$$u(C_P) = C_P \cdot \sqrt{\left(\frac{u(m_{\text{KH}_2\text{PO}_4})}{m_{\text{KH}_2\text{PO}_4}}\right)^2 + \left(\frac{u(P_{\text{KH}_2\text{PO}_4})}{P_{\text{KH}_2\text{PO}_4}}\right)^2 + \left(\frac{u(V_{1000})}{V_{1000}}\right)^2} \quad \text{Eq. 10}$$

The uncertainty of the working reference solutions ($u(C_{P-i})$) is associated with the uncertainty of the stock reference solution concentration ($u(C_P)$), the uncertainty of volumetric equipment, effect of temperature and repeatability of volume deliveries in preparation of the working reference solutions. The uncertainty due to repeatability of volume deliveries was included in the repeatability contribution for the overall experiment. The method has two dilution steps (dilution factor f_{ds} and dilution factor f_{d} .

i.); the uncertainty of each step was calculated from the uncertainty of the volumetric equipment and the uncertainty associated with the use of volumetric equipment at temperatures different from that of calibration, similar to that described above.

The concentration of n working reference solutions ($C_{P-1}, \dots, C_{P-i}, \dots, C_{P-n}$) was calculated using the equation:

$$C_{P-i} = C_P / (f_{ds} \cdot f_{d-i}) \quad \text{Eq. 11}$$

where C_P is the concentration of stock reference solution, f_{ds} is the dilution factor of the first dilution step and f_{d-i} is the dilution factor of the second dilution step for preparation of each reference solution ($f_{d-1}, \dots, f_{d-i}, \dots, f_{d-n}$).

The uncertainties of working reference solutions were calculated as:

$$u(C_{P-i}) = C_{P-i} \cdot \sqrt{\left(\frac{u(C_P)}{C_P}\right)^2 + \left(\frac{u(f_{ds})}{f_{ds}}\right)^2 + \left(\frac{u(f_{d-i})}{f_{d-i}}\right)^2} \quad \text{Eq. 12}$$

The standard uncertainties of the absorbencies ($A_1, \dots, A_i, \dots, A_n$) of standard solutions and of the absorbance of the sample (A) were estimated as the standard deviations of the mean of replicate determinations of each measurement of absorbance.

The standard uncertainty of the sample dilution factor (F_{dil}) was estimated from the uncertainty of the volumetric equipment and the uncertainty associated with the use of volumetric equipment at temperatures different from that of calibration, similarly as described above.

Uncertainty associated with repeatability

All steps of the measurement procedure included the uncertainty associated with the repeatability of the experiment. All repeatability contributions such as the repeatability of volume deliveries in preparation of working reference solutions and the repeatability of volume deliveries of sample were combined into one contribution for the overall measurement procedure and the uncertainty associated with repeatability was determined experimentally ($u(F_{rep})$).

Uncertainty associated with homogeneity

The standard uncertainty associated with the homogeneity of the sample, $u(F_h)$, was determined experimentally analysing different batches of samples. The between batch variation was expressed as the standard deviation after subtraction of the uncertainty of the analytical procedure.

Uncertainty associated with storage conditions

The uncertainty associated with the effect of storage conditions $u(F_s)$ on the results was determined experimentally. The samples were preserved by acidification to pH 1 with sulphuric acid, stored in the dark at temperature between 2 °C and 5 °C and analysed periodically. Maximum time frame covered with this experimental determination was three months. The uncertainty associated with the storage conditions was expressed as the standard deviation after subtraction of the uncertainty of the analytical procedure.

Uncertainty associated with recovery

The recovery of the analyte from the matrix is affected by the composition of the matrix. A spike was used to estimate the recovery of the analyte from the sample and the uncertainty associated with recovery ($u(F_r)$) was calculated as the standard deviation.

Calculation of combined and expanded uncertainty

The uncertainty of P_{tot} was estimated by combining the standard uncertainties of A , A_i ($A_1, \dots, A_i, \dots, A_n$), C_{P-i} ($C_{P-1}, \dots, C_{P-i}, \dots, C_{P-n}$), F_{dil} , F_{rep} , F_h , F_s and F_r . Uncertainties were combined by using the rule for propagation of errors^{2,6}.

Generally, the result of a measurement is determined from other quantities and the relationship between result y and the values of the input parameters can be expressed by a model:

$$y = f(x_1, x_2, \dots, x_i, \dots, x_N) \quad \text{Eq. 13}$$

where $x_1, \dots, x_i, \dots, x_N$ represent model input parameters. ($A, A_1, A_2, \dots, A_n, C_{P-1}, C_{P-2}, \dots, C_{P-n}, F_{dil}, F_{rep}, F_h, F_s, F_r$). The uncertainty of the result ($u(y)$) depends on the uncertainty of the input parameters and is described by the equation:

$$u(y)^2 = \sum_{i=1}^N \left(\frac{\partial y}{\partial x_i} \right)^2 \cdot u(x_i)^2 \quad \text{Eq. 14}$$

where $u(x_i)$ are the standard uncertainties of the input parameters, and $\partial y / \partial x_i$ is a sensitivity coefficient. The sensitivity coefficient describes how the measurement result varies with changes in the value of input estimates. Equation 14 is valid for measurements where there is no correlation between input parameters.

To calculate the expanded uncertainty of the result of measurement at the 95% confidence level, the result for combined uncertainty was multiplied by a coverage factor of 2.

Relative uncertainty variance contributions are used to illustrate the relative impact of different uncertainty components. The relative contribution (r_i) of an uncertainty component x_i to the combined standard uncertainty is defined here as:

$$r_i = \frac{\left(\frac{\partial y}{\partial x_i} \right)^2 \cdot u(x_i)^2}{u(y)^2} \quad \text{Eq. 15}$$

where y is the model equation ($y=f(x_1, x_2, \dots, x_i, \dots, x_N)$), x_i are input parameters of the model ($A, A_1, A_2, \dots, A_n, C_{P-1}, C_{P-2}, \dots, C_{P-n}, F_{dil}, F_{rep}, F_h, F_s, F_r$) and where $u(y)^2$ is the combined uncertainty calculated according to equation 14.

Results and discussion

The values of input estimates with their respective standard uncertainties, sensitivity coefficients and types of standard uncertainty evaluations are given in Table 1.

The relative contributions (r_i) from uncertainties of input parameters ($u(A), u(A_1), u(A_2), u(A_3), u(A_4), u(A_5), u(A_6), u(C_{P-1}), u(C_{P-2}), u(C_{P-3}), u(C_{P-4}), u(C_{P-5}), u(C_{P-6}), u(F_{dil}), u(F_{rep}), u(F_h), u(F_s), u(F_r)$) are presented in Figure 2.

The result of measurement was 0.215 mg/l, and the evaluated combined uncertainty was 8×10^{-4} mg/l. To obtain an expanded uncertainty at the 95% confidence level, the combined uncertainty was multiplied by the coverage factor k of 2. Therefore the expanded uncertainty of the result of measurement was 0.215 ± 0.0016 mg/l (0.7%). This evaluated uncertainty is comparable with the experimentally determined variation based on control charts (0.9%). The largest contributions come from $u(A)$ and $u(F_{\text{rep}})$ which contribute 60% to the combined standard uncertainty variance. The other contributions are of minor importance. Measurement uncertainty could be reduced most effectively by increasing the number of replicates.

Table 1 Uncertainty components and their relative standard uncertainties

| Quantity | Symbol | Unit | Value | Standard uncertainty | Sensitivity coefficient | Type of estimation |
|--|----------------|------|--------|----------------------|-------------------------|--------------------|
| Absorbance of the sample | A | | 0.1230 | 3.3×10^{-4} | 1.40 | Type A |
| Absorbance of the reference solution C ₁ | A ₁ | | 0.0276 | 4.9×10^{-4} | 0.27 | Type A |
| Absorbance of the reference solution C ₂ | A ₂ | | 0.0563 | 5.6×10^{-4} | 0.26 | Type A |
| Absorbance of the reference solution C ₃ | A ₃ | | 0.0856 | 6.2×10^{-4} | 0.25 | Type A |
| Absorbance of the reference solution C ₄ | A ₄ | | 0.1430 | 6.8×10^{-4} | 0.23 | Type A |
| Absorbance of the reference solution C ₅ | A ₅ | | 0.2326 | 4.9×10^{-4} | 0.19 | Type A |
| Absorbance of the reference solution C ₆ | A ₆ | | 0.2895 | 6.2×10^{-4} | 0.17 | Type A |
| Concentration of the reference solution C ₁ | C ₁ | mg/l | 0.0400 | 4.0×10^{-4} | 0.20 | Type B |
| Concentration of the reference solution C ₂ | C ₂ | mg/l | 0.0800 | 4.0×10^{-4} | 0.19 | Type B |

Table 1 Continued.

| Quantity | Symbol | Unit | Value | Standard uncertainty | Sensitivity coefficient | Type of estimation |
|--|------------------|------|--------|----------------------|-------------------------|--------------------|
| Concentration of the reference solution C ₃ | C ₃ | mg/l | 0.1200 | 4.2×10^{-4} | 0.18 | Type B |
| Concentration of the reference solution C ₄ | C ₄ | mg/l | 0.2000 | 4.7×10^{-4} | 0.16 | Type B |
| Concentration of the reference solution C ₅ | C ₅ | mg/l | 0.3200 | 5.6×10^{-4} | 0.14 | Type B |
| Concentration of the reference solution C ₆ | C ₆ | mg/l | 0.4000 | 6.5×10^{-4} | 0.12 | Type B |
| Dilution factor | F _{dil} | | 1.2500 | 8.5×10^{-4} | 0,17 | Type B |
| Repeatability | F _{rep} | | 1.000 | 2.5×10^{-3} | 0.17 | Type A |
| Homogeneity | F _h | | 1.000 | 1.2×10^{-3} | 0.17 | Type A |
| Storage conditions | F _s | | 1.0000 | 7.5×10^{-4} | 0.17 | Type A |
| Recovery | F _r | | 1.0000 | 7.5×10^{-4} | 0.17 | Type A |

In the present study all uncertainty sources were included in the calculation of combined measurement uncertainty. In routine calculation of measurement uncertainty all components smaller than one third of the largest one have no significant influence on the final result and can be neglected. For the purpose of this paper, all sources were taken into account and discussed in order to assess the implications of each of the uncertainty components and their influence on the final result.

For the selected case presented here, measurement uncertainty was calculated for one single determination of total phosphorus in a wastewater sample. The magnitudes of uncertainty components vary with the concentration level of the measurand and in further studies it is important to take into account the changes in the combined standard uncertainty with the level of the measurand by restricting the specified procedure to a small range of measurand concentrations.

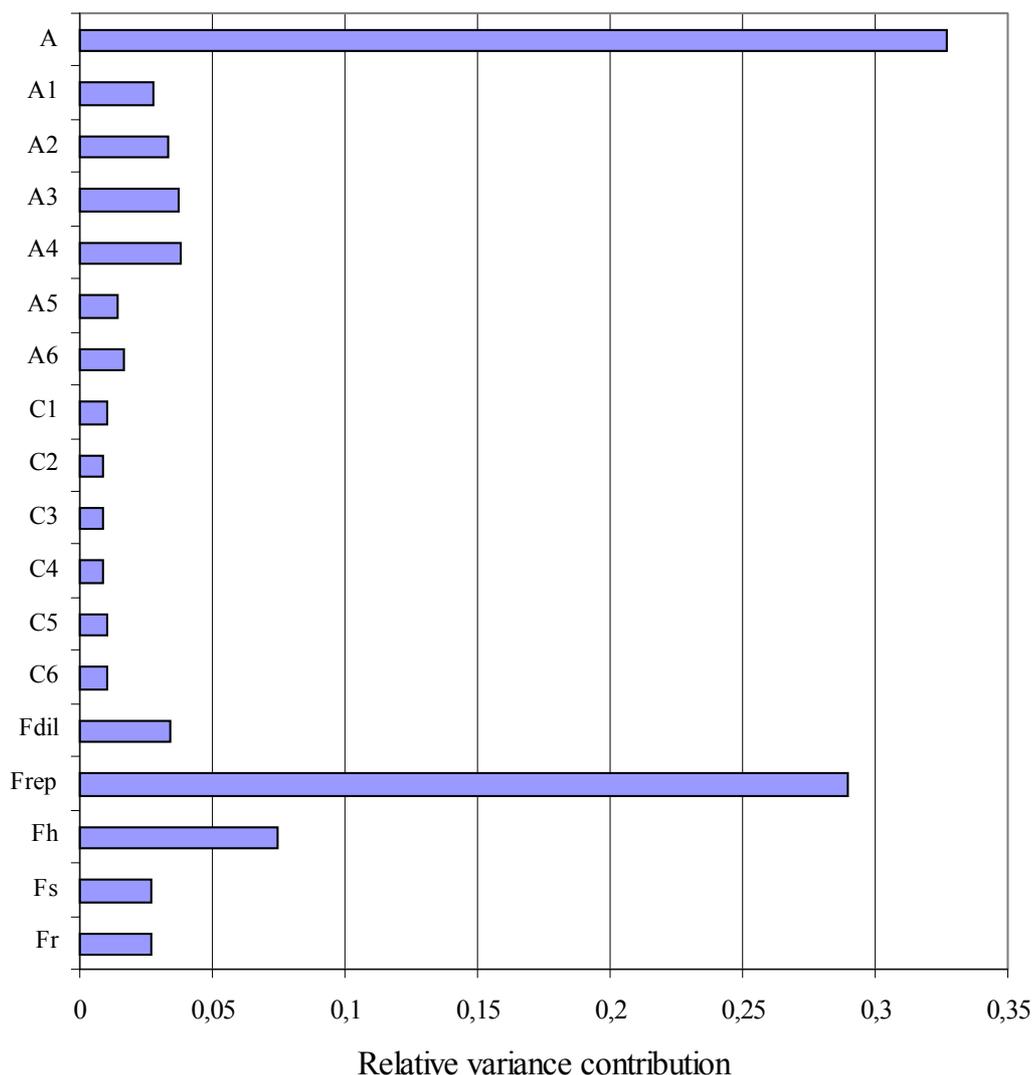


Fig. 2 Relative contributions from input parameters to the combined uncertainty variance $u(P_{\text{tot}})^2$

Conclusions

Detection of the major uncertainty components offers a tool for improving the performance of the determination. Systematic uncertainty budgets, such as the design presented here, facilitate the uncertainty evaluation process and makes it easier to compare contributions of uncertainty components to the total uncertainty budget, as well as promoting performance improvement of the method.

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Povzetek

Ovrednotili smo merilno negotovost rezultata meritve celotnega fosforja v vzorcu odpadne vode po spektrofotometrični metodi z amonijevim molibdatom. Identificirali smo glavne vire negotovosti rezultata meritve: linearna kalibracija po metodi najmanjših kvadratov, faktor razredčenja, ponovljivost, homogenost vzorca, pogoji hranjenja vzorca in izkoristek. Identifikaciji in ovrednotenju virov negotovosti je sledil izračun kombinirane merilne negotovosti. Rezultati so pokazali, da glavni vir negotovosti izvira iz kalibracijske premice, katera je ciljna operacija za izboljšanje izvajanja metode.