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Monte Carlo bottom-up evaluation of the uncertainty of quantification of heavy metals analysis in acid mine drainage by ICP-OES

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ABSTRACT

Many instrumental quantifications for heavy metals require the establishment of the calibration curve between calibrator's signals and mass concentrations based on linear regression model. However, linear fitting based on the ordinary least squares regression model faces the challenges from the instruments, such as homoscedasticity of signals, which may result in the poor performance for the measurement of low mass concentration. In comparison, the linear weighted regression model in many studies has been proven to better address the problem of heteroscedasticity in inductively coupled plasma emission spectrometer (ICP-OES). This study developed a computational software incorporating the linear weighted regression model for the bottom-up evaluation of the measurement uncertainty from a few replicate signals of calibrators and sample. It includes a model of signal precision variation in calibration interval based on the adjustment factor from the previously detailed and daily calibration. In addition, normal distribution for signal repeatability in ICP-OES was confirmed by using the Jarque-Bera test. The Monte Carlo method (MCM) employed here is designed for simplicity and intuitiveness, thus minimizing complex mathematical maneuvers, although it does presuppose a basic proficiency in computer programming. The method was successfully applied to assess the mass concentration of heavy metals (Cu, Zn, Fe, and Mn) in acid mine drainage by ICP-OES after necessary sample dilution. The robustness of developed measurement uncertainty method, which will not be limited by this assumption of the quality of calibrators preparation, was validated through the analysis of control standards with known mass concentration and sample with several spiking levels. The metrological compatibility of mass concentration and respective uncertainty was given to show the feasibility, practicality and reliability of the MCM simulations. A user-friendly software for the MCM is provided in the supplementary material. Overall, this study makes a contribution to the objectivity of the evaluation of environmental sample analysis.

1. Introduction

Acid mine drainage (AMD) has been recognized one of the most serious potential risks of environmental pollution in both operating and abandoned polymetallic sulfidic mines [1–3], and has attracted widespread attention from various international organizations, scientific communities, and civil groups. It is commonly considered as an extremely acidic wastewater with elevated concentration of heavy metals (e.g., Cu, Zn, Fe, and Mn). These heavy metals, mainly released from oxidation of sulfide-rich minerals in the surface weathering area, may contaminate surface and groundwater and soils, and finally damage the health of plants, wildlife, and humans through the food chain [4,5]. Most researchers published concentrations of heavy metals in acid mine drainage at contaminated area, and debated their source and migration in the water and sediments [6], in which most of quantitative data are obtained from inductively coupled plasma emission spectrometer (ICP-OES) [2,7,8]. Up to now, this instrument is an available tool for determining various heavy metals in trace level from complex water matrices, because of their accuracy and selectivity. However, it is still lack of uncertainty evaluation associated with quantification of the pollution, influencing objectivity in comparison of similar contamination levels.

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Quality of test data can be characterized by the uncertainty of measurement, which is crucial for determining whether the results fulfill the purpose and provide a reliable interpretation. However, an accurate evaluation of the measurement uncertainty of heavy metals by ICP-OES throughout calibrator and sample's preparation remains challenging. The complexity persists despite a few studies examining the impact of both random and systematic errors on the measurements obtained from various instruments [9–16]. The principles for bottom-up uncertainty evaluation require that all factors resulting in the discrepancy between the conventional 'true' value and measured value are taken into account based on the Guide to the Expression of Uncertainty in Measurement (GUM) [17,18]. Evaluation from the GUM quantify and combine uncertainty sources assuming a linearized propagation of the uncertainty components and components' independence. Subsequently, acquisition of the expanded uncertainty requires the calculation of the effective degrees of freedom based on the Welch–Satterthwaite formula. But it cannot exactly coincide with the actual measurement, which is the results of the complexity of measurement model and correlation among multiple contributory factors [19,20]. As a supplement, the Monte Carlo method (MCM) constructs a mathematical calculation which requires random and repeated sampling of probability density functions (PDF) of the input variables to generate a distribution for the output variables. The measurement uncertainty can be programmed for calculation by extracting optimal estimation from such output variables at a certain confidence level (e.g., 2.5th and 97.5th percentile vs. 0.5th and 99.5th percentile) after the establishment of the probability density distribution of the results. Various PDF distributions, such as rectangular, triangular, normal, and Student's t, are commonly adopted in evaluation of uncertainty of the measured quantity for the input quantities [21]. 10,000 to 100,000 calculations are considered to be satisfied with acquisition of stable estimates for many instrumental measurements.

Currently, the MCM has been used to evaluate measurement uncertainty of analytical instrument involving in calibration curves established on the ordinary least squares regression model (LSRM) [14,22,23]. For example, Dadamos do et al. [9] developed a MS-excel file for the Monte Carlo uncertainty evaluation of instrumental quantifications where LSRM is used for the extrapolation of the calibration curve in the cumulative standard addition method. Producing reliable measurement quantifications in the evaluation must meet the assumptions of LSRM-1) The linear correlation between calibrations and instrumental responses; 2) The homogeneity of variances from instrumental responses; 3) The irrelevance of the uncertainty of quantity values of any pair of calibrators given instrumental signal precision. However, the last two items have been proved to particularly inapplicable for many instruments of trace element analysis (e.g., Inductively coupled plasma mass spectrometry, Inductively coupled plasma optical emission spectrometry, and Atomic absorption spectroscopy), which result in a poor regression fit, and, therefore, incorrect quantification [9,13,14,21]. Additionally, negligence of calibrators' preparation and absence of selecting the probability distribution which best fits to repeatable instrument signals in some researches may generate the artificial bias for the uncertainty evaluation [9,13]. In comparison, linear weighted regression model (LWRM) has access to deal with approximate heteroscedastic data without the prerequisites of constant signals variance, and is in favour of improvement of the accuracy in quantitative measurement [22]. It is also programmed into commercial quantitative software of ICP-OES, which always weight the influence of each measurement by the inverse of the variance of instrumental signals. Although it has not been discussed in literature to date, we expect to assess the measurement uncertainty by MCM even in the case of heteroscedastic data.

Overall, in ordering to obtain the comparable data at similar concentration levels for global studies on acid mine drainage, it is necessary to perform the evaluation of quality of test data from ICP-OES. Furthermore, heteroscedastic instrument signals in calibrators at the several concentration levels should be taken into consideration for linear regression, although intense linear correlation exists. The LWRM has more significant advantages in operation of heteroscedastic data and quantification for low concentration sample than the LSRM. Therefore, this study develops a methodology applying to the determination of heavy metals in acid mine drainage by ICP-OES, and performs a MCM bottom-up evaluation of instrumental quantification based on the LWRM. Combined with the defined uncertainty model, we also compare the values obtained from references, standard curve method, standard addition method, and MCM in terms of metrology. The established signal precision model successfully reduces the demand for collecting many replicate signals during the calibration interval for the uncertainty evaluation, which conforms to the measurement reality. The achievement of precision model requires a factor that adjusts the previously estimated signal standard deviation to daily precision conditions. In this study, a variety of factors for calibrators' preparation uncertainty and the probability density function of the ICP-OES signals are considered to input the MCM simulation. Supplementary Material contains a user-friendly tool for evaluating instrumental quantifications based on calibrations using the LWRM model.

2. Materials and methods

2.1. Reagents, reference materials, and sample preparation

All chemical preparations were carried out in the class-100 laminar flow hoods in a class-1000 ultraclean room at the State Key Laboratory of Nuclear Resources and Environment, East China University of Technology, in Nanchang, China. Calibrators and control standards for Cu, Fe, Mn, and Zn were prepared using the respective commercially available reference materials (aqueous NACIS ICP standard solutions, China): Cu [1000 ± 5.0] mg L^{-1}, Fe [1000 ± 5.0] mg L^{-1}, Mn [1000 ± 5.0] mg L^{-1}, and Zn [1000 ± 5.0] mg L^{-1}. Their expanded uncertainties were obtained with a coverage factor of 2 and are within a 95 % confidence level. Ultrapure water (18.2 MΩ cm^{-1}) was obtained from laboratory tap water using an ELGA purification system (Maxima USF ELGA, High Wycombe, United Kingdom). Guaranteed nitric acid 69 % was purchased Sinopharm Chemical Reagent Co., Ltd., China, and was distilled with Savillex DST-1000 purification systems (America) prior to use. Ultra-pure water was used in preparation of solutions after acidification with nitric acid. Acid mine drainage (H-3) was sampled from the Chengmenshan Cu–Au deposit (Jiangxi province, Southeast China), and acidized with nitric acid. Possible suspended particles in samples were excluded from the sample solution using 0.20-m disposable syringe filters purchased from Tianjin Fuji Science&Technology Co., Ltd. (China).

The calibrators for the analysis of multi-elements through ICP-OES spectrometer were obtained from the preparation of mixed standard scales, including Cu [0–16] mg L^{-1}, Fe [0–16] mg L^{-1}, Mn [0–16] mg L^{-1}, and Zn [0–16] mg L^{-1}. In this study, five calibration intervals were employed for standard curve method. Quality control samples were prepared with the following mass concentrations: Cu [1.00 ± 0.01] mg L^{-1}; [2.50 ± 0.03] mg L^{-1}, Fe [1.00 ± 0.01] mg L^{-1}; [2.50 ± 0.03] mg L^{-1}, Mn [1.00 ± 0.01] mg L^{-1}; [2.50 ± 0.03] mg L^{-1}, and Zn [1.00 ± 0.01] mg L^{-1}; [2.50 ± 0.03] mg L^{-1}. Details of the dilution procedure are shown in Fig. 1. The dilution involves in calibrated micropipettes (100 μL–1000 mL, 1000 μL–5000 μL, and 1000 μL–50,000 μL) and class A volumetric flasks (50 mL). Operating temperatures for laboratory tests are between 18 °C and 22 °C. Also, mass concentration in the acid mine drainage is determined by addition of the estimated mass concentration γ (mg L^{-1}) at 3 interval level in the diluted solution with known coefficient of dilution.

2.2. Instrumentation and validation procedure

The instrumental quantifications were performed in an agilent 5110 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) at the State Key Laboratory of Nuclear Resources and Environment, East China University of Technology, in Nanchang, China. The ICP operating

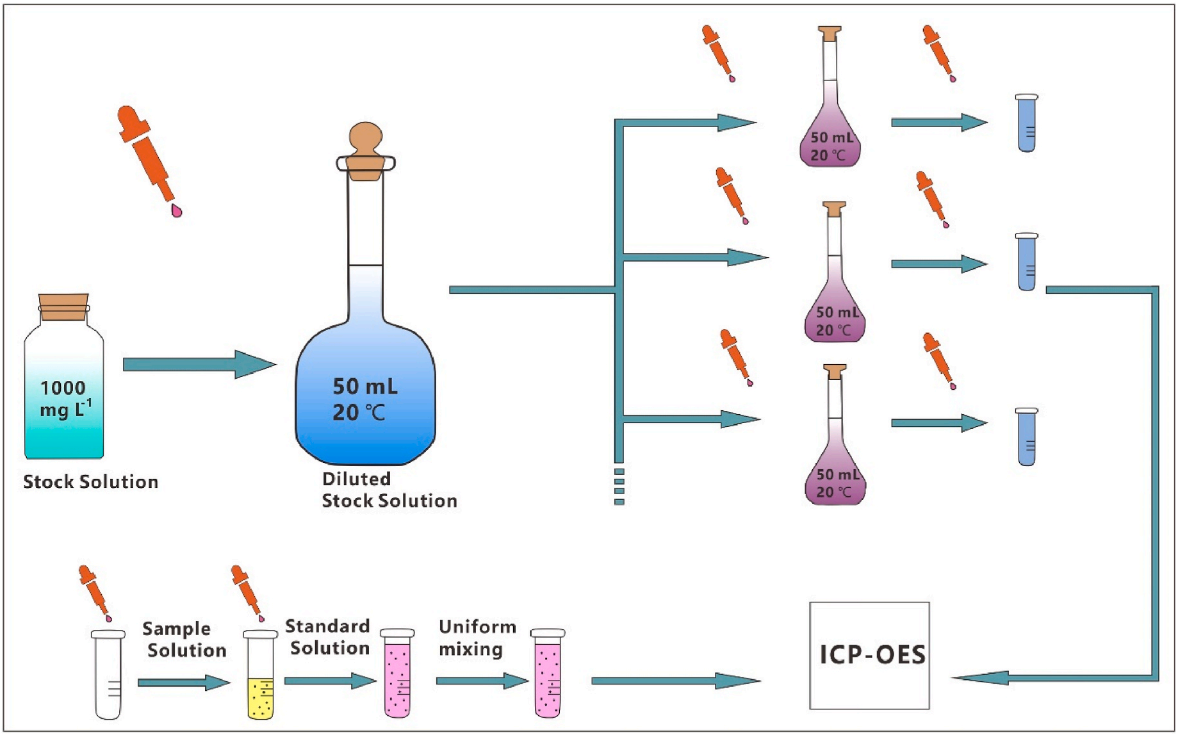

Fig. 1. Scheme of calibrators, control standards, and spiked samples preparation procedure.

conditions are listed in Table 1. Element emission lines were 324.754 nm for Cu, 234.350 nm for Fe, 260.568 nm for Mn, and 202.548 nm for Zn.

Before the measurement uncertainty evaluation and acid mine drainage analyses, the ICP-OES analytical routine was requested for checking signal linearity, limit of detection, limit of quantification, and signal repeatability. The validation procedure also involves in comparison between target (i.e. maximum admissible) uncertainty and the estimated measurement uncertainty which are combined by the Monte Carlo method. During the measurement of element mass concentration, the signal intensity of each calibrator and sample is obtained through the mean of triplicate readings of a stationary signal response. In order to ensure instrumental linearity and define a model of signal repeatability variation in detail, 20 replicate signals of each calibrator and sample were collected in the previous calibration day. Obtained signal values were reported at a 99 % confidence level after elimination of outliers by the Grubbs test [24,25]. The assumption of homoscedasticity can lead to a poor regression fit that is remarkable in the lower concentration level for the ordinary least squares regression model. Owing to its application of weighted least square method [13,26,27], homoscedasticity test of variance is abandoned in this study (Fig. 2). In turn, T test and determination coefficient of the linear correlation (R^2) are conductive to visually assess goodness of fit of the model and is adopted in this study.

Table 1
ICP instrumental parameters for heavy metals measurement.

Operating specification	Parameters
RF power (W)	1300
Ar gas flow rates (L min^{-1})	Plasma: 15 Nebulizer: 1.5 Auxiliary: 0.75
Solutions uptake rate (L min^{-1})	1.5
Peristaltic pump rotation speed (rpm)	20
Spectral line (nm)	Cu: 324.754 Fe: 234.350 Mn: 260.568 Zn: 202.548

3. Evaluation of measurement uncertainty by the Monte Carlo method

The MCM employs random number generations to solve the problems of linear model and asymmetry of propagation probability distribution in uncertainty evaluation for quantitative analysis. It avoids complex analytical mathematical description, instead relying on computer programming. Prior to implementing the MCM evaluation, all the input quantities values and their corresponding probability density function (e.g., rectangular, triangular, normal or student's t) are used to describe the uncertainty within a defined measurement model. Factors involving in systematic and random effects on the testing results should be taken into account wherever possible. Fig. 3 present an Ishikawa diagram represents the identified, quantified and combined uncertainty components, including mass concentration of the stock solution, sample and calibrators aliquot volume, diluted volume for sample and calibrators, volume variation from laboratorial temperature, signal precision, and the linear regression model. Table 2 lists the input quantities and the respective PDF used for the heavy metals' determination of the mass concentration by ICP-OES. The uncertainty sources from volumetric operation include temperature assuming a triangular distribution, pipettes assuming a triangular distribution, volumetric flask assuming a triangular distribution, repeatability assuming a student's t distribution (Table 2 and Supporting material). A normal distribution function is used in the evaluation of mass concentration in stock solution.

In this study, the Linear Weighted Regression Model (LWRM) is used to describe the instrumental response variation in the calibration intervals. Prior to quantitation, the linearity between signal values and mass concentrations is assessed by T test and determination coefficient (R^2). The mathematical model for measurement of heavy metals in acid mine drainage is shown as follows:

$$\gamma_0 = \gamma_1 \times \frac{V_0}{V_1} \ldots\ldots \quad (1)$$

$$\gamma_1 = \frac{\bar{I} - B}{A} \ldots\ldots \quad (2)$$

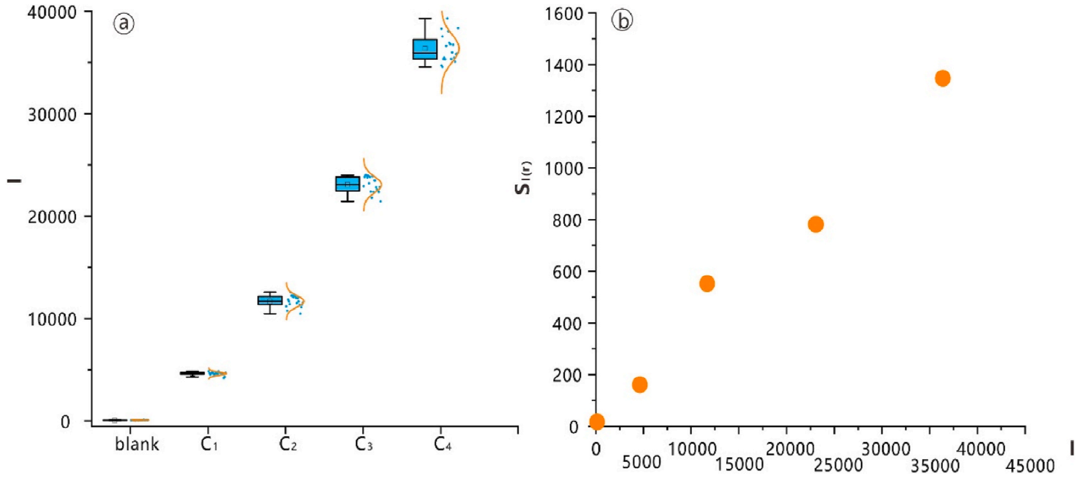

Fig. 2. (a) Binary plots showing signal value (I) as a function of mass concentration; (b) Binary plots showing repeatability standard deviation ($S_{I(r)}$) as a function of signal value (I), a case of Cu measurement by ICP-OES.

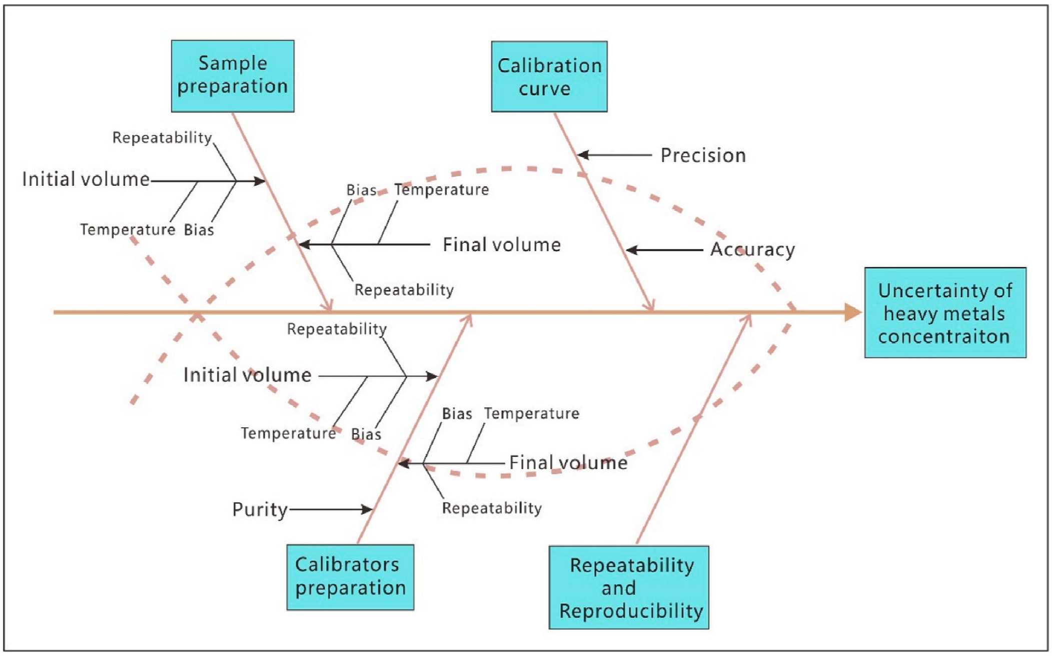

Fig. 3. Identification of the uncertainty sources throughout an Ishikawa diagram.

$$A = \frac{\left(\sum_{i=1}^{M} W_i\right)\left(\sum_{i=1}^{M} W_i I_i q_i\right) - \left(\sum_{i=1}^{M} W_i q_i\right) \times \left(\sum_{i=1}^{M} W_i I_i\right)}{\left.\sum_{i=1}^{M} W_i\right)\left(\sum_{i=1}^{M} W_i {q_i}^2\right) - \left(\sum_{i=1}^{M} W_i q_i\right)^2} \tag{3}$$

$$B = \frac{\sum_{i=1}^{M} W_i I_i}{\sum_{i=1}^{M} W_i} - A\frac{\sum_{i=1}^{M} W_i q_i}{\sum_{i=1}^{M} W_i} \tag{4}$$

$$R^2 = 1 - \frac{\left(\sum_{i=1}^{M} W_i\right)(I_i - (Aq_i + B))^2}{\left(\sum_{i=1}^{M} W_i\right)\left(I_i - \frac{\sum_{i=1}^{M} W_i I_i}{\sum_{i=1}^{M} W_i}\right)} \tag{5}$$

Where γ_0 is mass concentration (mg L^{-1}) in sample, V_0 is sample volume, V_1 is final volume after dilution in equation (1), γ_1 is mass concentration (mg L^{-1}) in test sample, _I is mean signal value from the instrument, A is slope of the calibration curve, B is intercept of the calibration curve in Equation (2), M is the total number of calibrators, W_i is the weighting factor of the i-th calibration interval level, I_i is mean signal value of the i-th calibration level, q_i is mass concentration (mg L^{-1}) of the i-th calibration level. The weighting methods for the regression method eliminate the influence of each series of data by the inverse of the variance ($1/I^2$) for the estimated measure of effect.

In order to overcome the limitation of collection of a large number of replicate signals (a minimum of six readings) of calibrators for assessing measurement uncertainty, a signal precision model is developed based on the observed variation of signals on several daily calibrations. The model for instrumental signals of calibrators requires the assumption of uniformity of heavy metals in sample solutions. For many instruments with high sensitivity, it presents a positive relationship between the

Table 2
Input probability distributions used to estimate the uncertainty of ICP-OES for determination of copper in acid mine drainage by the Monte Carlo method.

Input quantity	Symbol	PDF type	Unit	Value	U or u	υ
S0	γss	N	mg L^{-1}	1000	5	
C1-Pipette	Bias	TR	mL	2.0	0.015	
	Rep.	St			0.006	9
C2-Pipette	Bias	TR	mL	5.0	0.015	
	Rep.	St			0.011	9
C3-Pipette	Bias	TR	mL	10.0	0.021	
	Rep.	St			0.016	9
C4-Pipette	Bias	TR	mL	16.0	0.030	
	Rep.	St			0.022	9
CS1-Pipette	Bias	TR	mL	1.0	0.005	
	Rep.	St			0.001	9
CS1-Pipette	Bias	TR	mL	2.5	0.015	
	Rep.	St			0.0	9
Volumetric flask	Bias	TR	mL	50	0.06	
	Rep.	St			0.092	9
Temperature		TR	C	20	2	
Signals	Blank	N	cps	41.73		
				115.5		
	C1	N	cps	4198.96		
				4862.19		
	C2	N	cps	10463.77		
				12583.61		
	C3	N	cps	21439.13		
				23994.49		
	C4	N	cps	34554.69		
				39292.42		
	CS1	N	cps	2200.54		
				2526.8		
	CS2	N	cps	5647.86		
				6270.56		

Note: U or u-Expanded or standard uncertainty; N-Normal distribution; TR-Triangular distribution; St-student's t distribution; υ-degrees of freedom of the uncertainty.

standard deviation of signal values and mass concentration, and sudden decrease of the relative standard deviation of signal values from Limit of Detection to about two times the Limit of Quantification after that it maintains approximately constant. Consequently, the maximum observed standard deviation is often selected for conservative estimation, potentially leading to a significant overestimation of uncertainty. In this study, signal variation regular from the measured values is maintained in the linear weighted regression model. Owing to the variations of instrumental sensitivity and precision along with the day, the previous precision model used to the daily precision model with single or few replicate signals must be under the condition of repeatable measurement environment through the adjustment factor. It assumes that overall tendency of precision variation keep constant in the preparative calibrator on instrument responses. So, the factor is the ratios of the residual standard deviation of unweighted regressions between the daily calibration curve-$S_{I(D)}$ and the previous calibration curve-$S_{I(P)}$ in this study. During the daily calibration, the weighting factor of the first calibrator is selected as its standard deviation of signal values multiplying $S_{I(D)}/S_{I(P)}$, and is used for the daily calibration curve. For example, if the precision at a certain daily calibration is one third of which at the previous calibration, then $S_{I(D)}/S_{I(P)}$ will be 3.

Also, the input data of the repeatability standard deviation in the signal values ($S_{I(r)}$) of calibrators' interval level is estimated by extracting $S_{I(r)}$ by multiplying $S_{I(D)}/S_{I(P)}$. It is noteworthy that the precision model is not involved in the measurement of unknown sample (acid mine drainage) by standard addition method. Also, it is abandoned in the simulation of MCM for the spiked samples. Based on the above mathematic model, the whole flow scheme of Monte Carlo method of the uncertainty of quantification in this study is briefly described as follows: Firstly, the final mass concentration of calibrators and control standards (CS1 and CS2) is obtained by sampling from the variation of stock solutions, pipette, volumetric flask, and temperature (Table 2); Next, the instrument signals of them are sampled depended on original data, and the sampled signals are used for the establishment of equation from weighted least square linear regression. For example, we sample 20 repeated signals for each calibrator, and regard the average value as the expectation after Grubbs tests. The average value of sampling signals of the control standards is introduced into the equation to calculate the concentration; Also, instrument signals of the acid mine drainage should be repeat the above process to obtain the mass concentration on a daily calibration; In addition, the dilution ratio is sampled by the variation of pipette, volumetric flask, and temperature. Finally, one sample value is saved by performing the above procedure in the computer system. In this study, simulating 10,000 series of each variable allows to produce stable estimation of measurement values. It is suggested that 2.5th and 97.5th percentiles or 0.5th and 99.5th percentiles are required to assess the measured results at the confidence level of 95 % or 99 %, respectively. All MCM simulations in this study are processed based on MATLAB platform. In the end, the authors developed the model proposed in this study into software called EUIM (Evaluation of Uncertainty in Instrument Measurement). This software is designed specifically for researchers, engineers, and laboratory technicians, providing tools for in-depth quantitative assessment of uncertainties arising in instrument measurements. EUIM employs stochastic simulation methods to iteratively model experimental conditions and various uncertain influences within the measurement process, enabling users to determine the statistical properties and expected range of measurement uncertainties.

4. Results and discussion

4.1. Sampling of ICP-OES signal repeatability

The probability distribution of numerous input variables, including volumes, temperature, and mass concentration of reference materials, are employed for simulation of the measurement uncertainty on the basis of prior knowledge from the verification regulation of associated equipment or the reference material certificate. Comparatively, the random variables for ICP-OES signal repeatability are gained with the examination and calculation of multiple values for calibrators at each calibration level. In theory, the analysis of replicate measurements will be guarantee to yield a stable and reliable estimate of true probability distribution, reflecting a comprehensive and unbiased perspective. On the daily calibration, only triplicate readings of instrumental response in calibrators and control standards are regarded as insufficiency for providing an available assessment (Supporting material). The estimate is, therefore, accomplished by a collection of 20 times readings during stationary signal response on the previous calibration, which serves as examples for the Jarque–Bera test for normality [28,29]. Prior to such test, Grubbs tests is used to check for the presence of the outliers for single and paired at a 99 % confidence level [24,25], allowing for the detection and removal of outliers where applicable. Fig. 4 presents result of applying the Jarque–Bera test for Cu signals at each calibration level, suggesting that most data conform well to the normal distribution hypothesis. Therefore, the mean and standard deviation of the measured signals in calibrations and sample solutions were used to participate in the subsequent MCM. It suggests that the probability distribution of instrument signals may have a significant impact on the outcome of the uncertainty measurement. In the subsequent uncertainty evaluation by the MCM, we suggest that more samples solutions and calibrators sourced from a stock solution can be taken into consideration to obtain a more representative probability distribution.

4.2. Compatibility between results of simulation and objective analysis

The mentioned measurement protocols are suitable for a wide range of mass concentrations of heavy metals in environment samples, thus validating their applicability for this series of analyses. However, a few studies focus on the quantification of measurement uncertainty in the

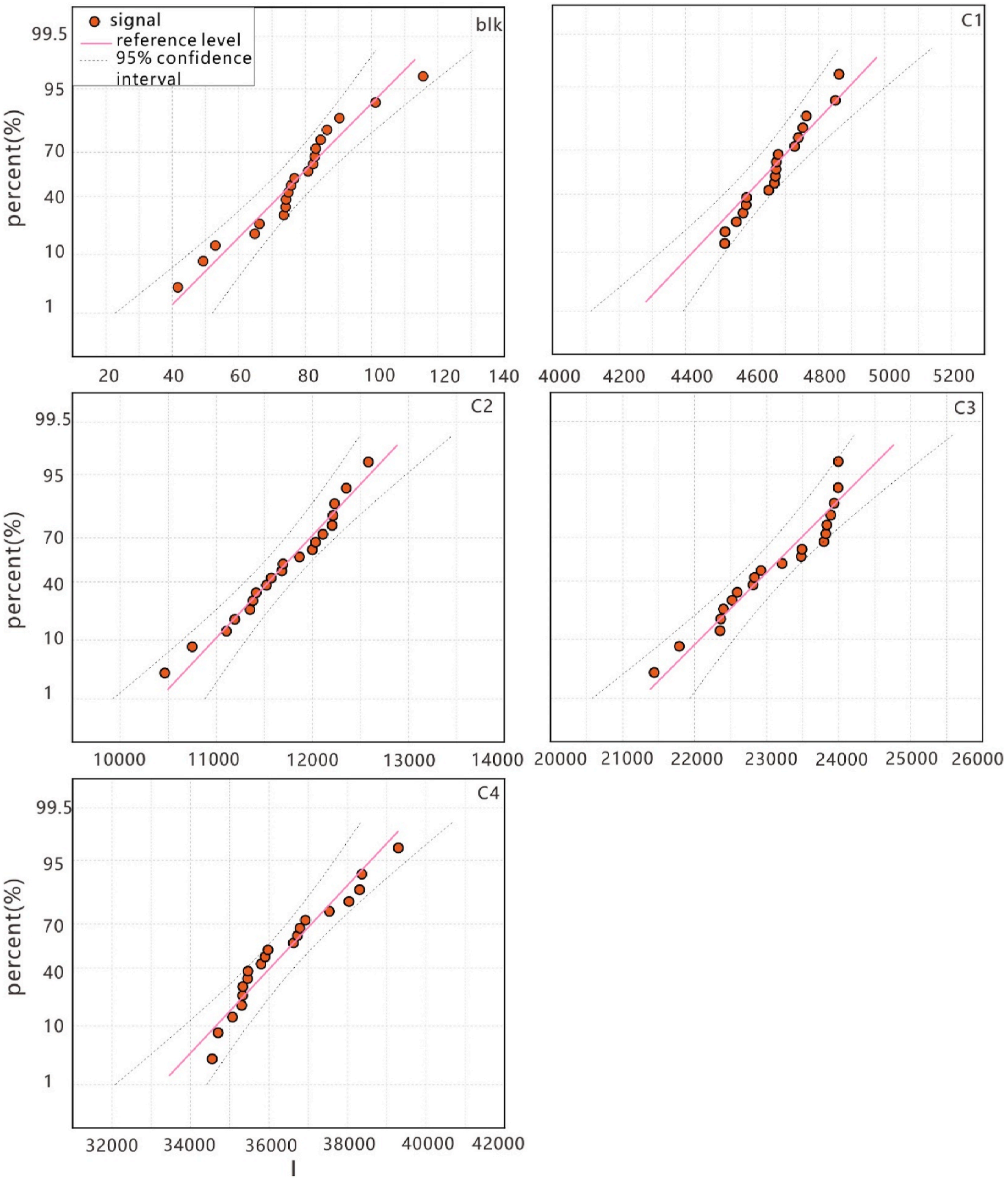

Fig. 4. Normal probability of all calibrators on the previous calibration day.

application of many instruments, indicating an area that warrants further investigation [8,28,30,31,32]. The established uncertainty evaluation model based on MCM, which focuses on instrumental signal precision, is validated through analysis of heavy metals (Cu, Zn, Fe, and Mn) in control standards and sample solution (acid mine drainage). All quantifications are carried out after instrument calibration with multiple readings. The procedure of evaluation begins with definition of quantity to be measured and the mathematic relation between the measured values and associated parameters (e.g., the input variables). The measurement model of heavy metals in acid mine drainage is defined by sample preparation, signal repeatability, signal precision, and selected linear regression model. During the measurement, all factors, including random and system effects, contribute to the measured quantity, producing the deviation between the obtained and true value. The sources of the uncertainty have been identified in Fig. 3. In addition, the distribution model of instrumental reading for ICP-OES has been analyzed in the above **Section 4.1**. 20 signal values are recorded on the previous calibration day at each calibrator and control standard, while 3 signal values on the daily calibration. Residual standard deviations from the previous calibrations ($S_{I(P)}$) and daily calibrations ($S_{I(D)}$) are important for the precision model. The preparation of all measurement solutions from a mixed stock solution ensures a more realistic simulation of the evaluated measurement uncertainties. The goodness of fit of signals and the mass concentrations of calibrators is checked by determination coefficient of the linear correlation (R^2), which draws a conclusion of positive correlation property between signals and the concentrations.

The quality of the measurement uncertainty model was evaluated by the metrological compatibility of mass concentration and respective uncertainty obtained from different approaches. If the following equation is valid, it can be concluded that the test results are metrologically compatible and equivalent.

$$|\mathrm{d}| = |\gamma_1 - \gamma_2| \leq k\sqrt{\mu^2(\gamma_1) + \mu^2(\gamma_2)} = k\mu(d) \tag{6}$$

Where γ_1 and γ_2 are mass concentration (mg L^{-1}) of the estimated and reference/spiked mass concentrations from the analysis of samples, respectively; $\mu(\gamma_1)$ and $\mu(\gamma_2)$ are the correspondent standard uncertainties, respectively; d and $\mu(d)$ are the value and standard uncertainty of the difference between the results from two approaches; The *k* is recommended to 2 or 3 for a compatibility test for the 95 % or 99 % confidence level, respectively.

If $|d| \leq k\mu(d)$, it can be concluded that the result is metrologically equivalent for the 95 % and 99 % confidence level. Otherwise, it is metrologically different.

Table 3 presents the results of the analysis of the estimated and reference control standard for a confidence level of 95 % for the measurement of Cu by ICP-OES, in which $\mu(\gamma)$ from the reference solution was expanded by a coverage factor of 2. It also reports the results of the uncertainty modelling by using the GUM(LWRM) and the MCM, respectively. The uncertainty of compatibility test was also expanded by a coverage factor of 2. The adjusting factor of daily precision calibration are $f = S_{I(D)}/S_{I(P)}$ used for MCM simulations. In addition, it is assumed that the standard deviation of simulations is regarded as respective measurement uncertainty in the case of a normal distribution, so that we allow to obtain the confidence interval through applying the law of propagation of uncertainty. The compatibility between results of the reference value and analysis of control standard based on the GUM (LWRM) suggests that the obtained mass concentration is valid. Also, the GUM(LWRM) and MCM evaluations are equivalent about the mass concentrations and expanded uncertainties of the studied 2 control standards for a 95 % confidence level, demonstrating equivalence of the measured uncertainty (Table 3). The slightly difference between the estimation from the GUM(LWRM) and MCM (e.g., 1.05 ± 0.27 vs. 1.05 ± 0.09 for CS1; 2.62 ± 0.26 vs. 2.61 ± 0.33 for CS2) can be the results of random number algorithm during the processing the Monte Carlo method. Fig. 5 shows the frequency distribution of simulated mass concentrations for the 2 control standards, which are overlapped the reference values.

Table 4 presents that the results of the analysis of the spiked sample for a confidence level of 95 % for the measurement of Cu by ICP-OES, in which $\mu(\gamma)$ from the different methods was expanded by a coverage factor of 2. The measurement uncertainty model is evaluated through the metrological compatibility in the standard curve method, standard addition, and MCM. It is observed to be metrologically compatible in both the measured values from different approaches, and suggest that the developed uncertainty models are available to predict the error of ICP-OES measurements in acid mine drainage. Fig. 6 presents the distribution of simulated mass concentrations for the sample H-3.

In summary, researchers without a programming background can use the evaluation software (EUIM) developed in this study, based on Monte Carlo simulations, to perform efficient assessments, with the entire evaluation process taking only a few minutes (Supporting material). Such evaluation result is regard as a reference for the quality of quantification and/or the comparative object from other evaluation methods. In addition, quantitative feedback of mass concentrations is provided in the computational results. In fact, other heavy metals (Mn, Co, and Ni) and elements (Na, K, Mg, Fe, and Ca) in environmental samples could be also determined by ICP-OES using LWRM as mathematical relationship between signals and mass concentrations. Application of the provided tool is suitable for the quantity evaluation of these elements.

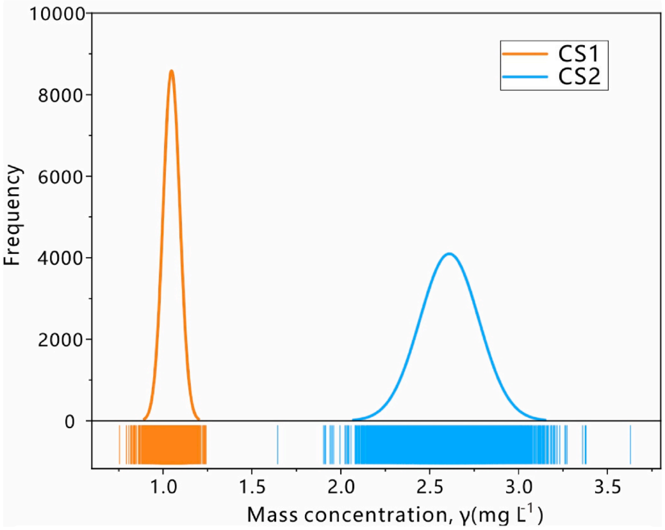

Fig. 5. Frequency distribution of simulated mass concentration in the two control standards.

Table 4
Measurement of the unknown sample (acid mine drainage) on a daily calibration.

Sample	Procedure	Measurement result	Compatibility test	K = 2	C/nC
H-3	Standard addition (GUM(LWRM))	5.53 ± 0.41		95 %	
	Standard addition (MCM)	5.53 ± 0.67	0.00 ± 0.78	95 %	C
	GUM(LWRM)	5.66 ± 0.50	0.13 ± 0.64	95 %	C
	MCM	5.63 ± 0.66	0.10 ± 0.77	95 %	C

Note: C or nC is compatible or not compatible measurements, respectively; Reference value was obtained from standard addition (LWRM) method.

5. Conclusions

The quantification of heavy metals (e.g., Cu, Zn, Fe, and Mn) of acid mine drainage by ICP-OES with an uncertainty model allows the objective comparison of different concentration levels. The signal precision model based on the combination between the previous and daily calibrations curve is established through the collection of a few replicate signals of calibrators and sample, and is introduced into the provided user-friendly tool for increasing efficiency in instrument quantification and evaluation of quality of reported data (Read the ‘User Manual for EUIM’ for more details). It adopts an adjustment factor of signal repeatability, which is calculated by the ratio between the residual standard deviations of the daily and previous calibration curves. Otherwise, the normal distribution hypothesis of signal repeatability is verified through the Jarque–Bera test, which is beneficial for sampling in the subsequent MCM. Linear weighted regression model with the inverse of the variance ($1/I^2$) of signal repeatability as the weighting

Table 3
Estimated and reference values of the analysis of control standards for a 95 % confidence level on a daily calibration.

Sample	Reference value	Procedure	Measurement result	Compatibility test	K = 2	C/nC
CS1	1.00 ± 0.01	GUM(LWRM)	1.05 ± 0.27	0.05 ± 0.27	95 %	C
		MCM	1.05 ± 0.09	0.05 ± 0.09	95 %	C
CS2	2.500 ± 0.03	GUM(LWRM)	2.62 ± 0.26	0.12 ± 0.26	95 %	C
		MCM	2.61 ± 0.33	0.11 ± 0.33	95 %	C

Note: C or nC is compatible or not compatible measurements, respectively.

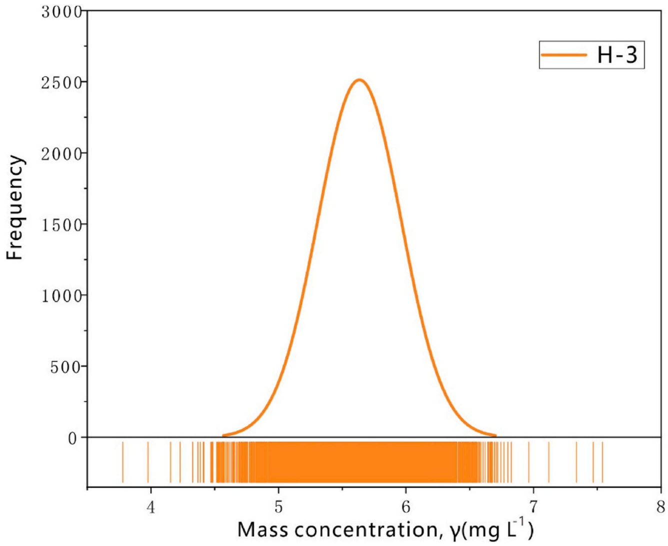

Fig. 6. Frequency distribution of simulated mass concentration in the sample (H-3).

factor is employed to deal with heteroscedastic signals reading from calibrators and samples. The metrological compatibility of mass concentration from other approaches is achieved to ensure availability of the developed methodology. Based on a few experimental data and prior probability distribution, we employee the Monte Carlo Method (MCM) to efficiently deliver a large number of results from experimental simulations until reaching a steady-state density squared distribution. EUIM statistics results in the mathematical expectation, variance, and range of values for the unknown sample at 95 % and 99 % confidence levels. In fact, the developed MCM allows a more widely application for the evaluation of instrumental quantification where the signal varies linearly with the concentration of calibrations. The user-friendly software of MCM simulation is in the Supplementary Material.

CRediT authorship contribution statement

Lin Xu: Writing – review & editing, Writing – original draft, Software, Methodology, Funding acquisition, Data curation, Conceptualization. **Pan Wang:** Software, Funding acquisition, Data curation. **Dandan Tang:** Data curation, Conceptualization. **Jianbin Xu:** Data curation, Conceptualization. **Chongguang Luo:** Writing – review & editing, Conceptualization. **Hanjie Wen:** Writing – review & editing, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2024.127315.

Data availability

Data will be made available on request.

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