Quantification of total mercury in samples from cement production processing with thermal decomposition coupled with AAS

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Abstract

This work aimed to assess the efficiency of a portable total mercury (Hg) analyzer (Lumex RA-915+) that employs direct thermal decomposition atomic absorption spectrometry (AAS) to liberate Hg from a sample matrix as well as validate the quantification method of total Hg in different materials that are used in cement production. Regarding the solid matrix of the samples, the approaches included matrix-matched certified reference materials (CRM) calibration and adding a standard calibration solution to the solid samples. While both calibration approaches were suitable for the instrumentation employed, the uncertainty of the Hg mass fraction in a CRM and the need to include several matrix CRMs that differed in analyte content added to the complexity of the case. Spiked calibration is an acceptable alternative to calibration because it provides a lower expanded uncertainty at 15 %, 15.5 %, and 21.7 %, for the highest (> 200 ng), middle (50–150 ng), and lowest (< 50 ng) concentration ranges, respectively, compared to matrix CRM calibration. The obtained expanded uncertainty, the minimal requirements for sample preparation, easy and straightforward calibration and measurement, and high sample output indicate that the quantification of total Hg with thermal decomposition coupled with AAS is suitable for materials that are used in cement production.

Keywords Total Hg · Uncertainty · Validation · Matrix-matched CRM · Calibration

Introduction

Mercury (Hg) is recognized as a global pollutant with a complex biogeochemical cycle, which has toxic effects on human health. Many national and international legal instruments aim to reduce Hg's release into immediate environments [1, 2]. In addition to natural sources of Hg that form background environmental levels, anthropogenic activities that are associated with the combustion of fossil fuels have increased the mobilization of Hg in the environment [3]. Major sources of Hg emissions continue to be energy production, the roasting and smelting of ores, cement production, ferrous and non-ferrous metals industries, etc. Cement

is among the cheapest and most ubiquitous materials that are used for construction, making it the second most used construction material in the world. Hg is introduced into cement production through raw materials and fuels. It is estimated that cement production contributes to approximately 10 % of all Hg emissions worldwide [4].

Among many analytical methods that are used for Hg measurements in environmental samples, those that employ direct thermal decomposition as a means of extracting Hg from a sample matrix with atomic absorption spectrometry detection (AAS) have the benefits of utilizing either few or none of the reagents, minimal requirements for sample preparation, fast analysis, and minimal analyte loss [5–8]. Quantitative analysis in spectrometric techniques produces results whose accuracy depends on the instruments' calibration to ensure comparability over time and among laboratories [9]. A vital component of comparability is the ability to calibrate instrumentation using traceable reference materials [10]. In most analytical techniques that are used for total Hg quantification, the calibration is performed with standards that are in an aqueous solution [11–13]. For total Hg quantification by thermal decomposition methods, where

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samples are analyzed in their solid form, calibration of the instrumentation with aqueous solutions would not consider the sample's matrix. Moreover, the difference in the physical form of the calibration standards and the samples leads to the difficult evaluation of metrological parameters [14]. The most appropriate action here would be to calibrate the instruments with reference materials that are of the same physical state as the studied samples [15]. This can be achieved by using certified reference materials (CRMs) of either the same or a comparable matrix to those of the samples.

A matrix-matched CRM that is used for calibration purposes must satisfy certain criteria: (1) the certified analyte content must be known with sufficient reliability, and (2) the CRM matrix must be similar to the samples [14, 16, 17]. An important feature in the use of a CRM for calibration purposes is the uncertainty regarding its analyte content because it is expected to influence the final uncertainty of the result [18]. The uncertainties in the matrix CRM are relatively large, and the decision to use them for calibration must be based on the target measurement uncertainty of the entire method [19]. Unfortunately, a cement CRM with appropriate Hg concentration is lacking, which led to difficulties in calibrating the instrument. To overcome this issue, a substitute approach was to add calibration solutions to the matrix of the samples ("spiked calibration" hereafter). This approach could be a suitable alternative because, during calibration, we were including the matrix of the considered sample, and the uncertainty of the calibration solution is much smaller compared to the matrix-matched CRM.

The objective of the present study was to evaluate the suitability of a direct thermal decomposition method for total quantification of the Hg in raw materials that are used for cement production. Two different approaches to calibration, which were described above, were employed in the research. Accordingly, the proposed method was validated, and the expanded uncertainty of the method was estimated.

Materials and methods

Instrumentation

Mercury analyzer RA-915M with a PYRO-915 + thermal decomposition attachment (Lumex Scientific, St. Petersburg, Russia) is based on differential Zeeman atomic absorption spectrometry using high frequency modulation of light polarization. The instrument is used for determination of total Hg by the manner of thermal decomposition, in various types of samples [20].

The working principle of the instrument is based on the thermal evaporation of Hg that is present in the sample. Using quartz boat, an aliquot of the sample is placed in the dosing unit of the first chamber of the atomizer that

operates at temperatures 680–750 °C using a gas flow rate of 0.8–1.2 L min⁻¹. The first chamber serves for decomposition of the solid samples, where Hg compounds are evaporated and dissociated to form the elemental Hg. Afterward, the gaseous compounds that are formed are transported into the second chamber of the atomizer, which is constantly heated at 800 °C to avoid Hg recombination with other oxidants, during which the complete combustion of the remaining volatile compounds takes place, where smoke and interference compounds are burnt. The Hg EDL (electrodeless discharge lamp) is placed in the gap between the poles of the magnet and is excited by the high frequency generator. The light successively passes through the polarization modulator to the optical bridge which automatically switches the light beam direction depending on the selected operation mode. In the external cell, which is used in this work, the radiation passes through the removable optical unit of the external analytical cell, then through the single-path cell compartment and arrives at the photodetector. Downstream from the atomizer, the airflow enters the detector where the absorption of the elemental Hg is detected at a wavelength of 253.7 nm. The photodetector signal reaches at the electronic signal-processing unit where it is separated at the modulation frequency and the analytical signal is formed. The whole decomposition procedure and detection of the Hg takes place in an enclosed system. The time that was required for the analysis ranged from 60 s to 180 s, depending on the mass of the sample and the Hg content.

The measurement procedure included weighing a portion of the sample (~0.1 g, Mettler Toledo AE 240 balance) in a quartz boat, which was afterward subjected to high temperatures in the combustion unit, where Hg was released quantitatively. The total area under the peak of the thermal release profile was considered an analytical signal for Hg quantification. After each measurement, the residue from the combustion is disposed and the quartz boat is "cleaned" by inserting it again in the combustion unit.

Reagents and samples

Raw mixtures that are used for cement production, such as limestone, a raw meal from different parts of the production process, clinker, and dust that has accumulated on air pollution control devices, were all materials of interest in this study. Apart from fuels, they represent the majority of the Hg-containing feed. For calibration and validation purposes, the following matrix CRMs were employed in this study (Table 1):

A solution of 5 % HNO₃ (v/v) was prepared prior dilution of standards and stored at room temperature (21 °C). This acid solution was used for the preparation of all standard dilutions. A new ampoule of Standard Reference Material NIST 3133, Mercury (Hg) Standard Solution

Table 1 Matrix CRMs that were used throughout the validation study

Certified reference materials	Total certified Hg with the stated uncertainties U ($k=2$) ng g^{-1}
NIST SRM 633a Portland Cement ^a	24.70 ± 0.81
ERM CC 141 Loam Soil ^a	83 ± 17
BCR 320R Channel Sediment ^a	850 ± 90
BCR 280R Lake Sediment ^a	1460 ± 200
BCR 277R Estuarine Sediment ^a	128 ± 17
NIST SRM-3133 Mercury (Hg) Standard Solution ^b	9954000 ± 53000

^aDry weight^bLot no. 061204

(Lot No. 061204), was gently shaken for 2 min and opened according to the certificate. The stock standard solution ($100 \mu\text{g mL}^{-1} = 97800 \text{ ng g}^{-1}$) was prepared by transferring $937 \mu\text{L}$ of SRM NIST 3133 solution with the pipette to a 100-mL glass flask containing 70 mL of previously prepared 5 % HNO_3 acid solution, stirred, and topped up with the same acid solution to the mark. The flask was then capped, well shaken and left on room temperature for 1 h before preparing further dilutions. The same principle was applied for the preparation of other concentrations (100, 500, 1000, 5000, 10000, 50000 ng mL^{-1}).

All pipettes were calibrated prior to use by weighing the appropriate volumes of Milli-Q water for 10 times at 20°C (density of Milli-Q water was taken from literature). The exact densities of the NIST 3133 solution and its dilutions were determined separately by weighing three aliquots using calibrated pipettes. All volumes described above (pipettes, glass flasks) were weighed on the balance at the same time to calculate exact mercury concentration on mass basis. The prepared solutions were kept at a constant temperature (21°C). The uncertainty of the volumes (pipettes, glass flasks) and expected variations in the temperature ($\pm 4^\circ\text{C}$) were included in the uncertainty budget.

Experimental setup and validation of the method

Calibration of the instrument

Two different approaches were employed to calibrate the output signal of the instrument by introducing known quantities of Hg. The relationship between a known amount of Hg and the output signal was represented by a calibration curve, which was constructed by plotting the absolute amount of Hg (ng) versus the integrated absorbance.

Calibration with the matrix CRM The external calibration of the instrument was conducted by weighing different portions of the matrix CRM. Under the influence of the high temperature in the pyrolyser, vapors of elemental Hg were

transported into the analytical cell, with background absorption being eliminated by the high-frequency Zeeman correction system. The absolute mass of the Hg (ng) was calculated from the relationship between the certified value of the Hg content in the matrix CRM and the mass (mg) that was used for calibration. Each point of the calibration curve consisted of four repeated measurements, although it was practically impossible to accurately weigh the same mass more than once. The plotting of the absolute Hg mass was done by correcting for moisture content.

Spiked calibration For the second approach to calibration, $\sim 0.1 \text{ g}$ of the sample (both NIST SRM 633a Portland Cement and real samples were used in this approach) was weighed. The naturally present Hg in this portion was firstly released quantitatively and then measured for blank. When it was assured that all the Hg was released, and the material was cooled down to the ambient temperature, it was spiked with the Hg^{2+} calibration solution. Afterward, the portion was again subjected to high temperatures in the pyrolyser, and the instrument's signal was recorded. Calibration solutions were prepared in different concentrations to obtain the proper working range as well as to keep the material's moisture at a minimum. Each calibration point consisted of four repeated measurements.

Validation parameters

The reliability of the measurement depends on the methods, which provide qualitative, reliable, and consistent results, with the final goal being a result that is close enough to the unknown true value of the content of the analyte in the sample. In this context, the parameters that were used for method validation included the following: calibration curve and working range, linearity, the LOD, the limit of quantification (LOQ), recovery, precision (repeatability and intermediate precision), as well as combined and expanded uncertainty of the result. Combined standard uncertainty, which considers

Fig. 1 Fish-bone diagram of all relevant sources of uncertainty in the determination of Hg content. **a** With matrix CRM calibration, **b** with spiked calibration

all uncertainty components in a complex measurement process, was calculated by combining the relative standard uncertainties of the major contributors during measurement, as presented in Fig. 1a, b. The expanded uncertainty in the final result consists of the combined standard uncertainty (u_c) multiplied by a coverage factor of $k = 2$.

Validation experiments were performed over an extended period, and the results were used to evaluate different validation parameters. The absolute LOD and LOQ were obtained from the elements of the regression function—the standard error of the intercept and the slope. Correspondingly, the LOD was calculated as three times the standard error of the intercept divided by the value of the slope, and the LOQ was ten times the standard error of the intercept divided by the slope. The repeatability included a contribution from any part of the procedure that varied within a run, including those from gravimetric errors. Five subsamples were measured three times during the day, and repeatability standard

deviation was calculated. The evaluation of intermediate precision was carried out by analyzing three samples that corresponded to three different concentration levels on different days. A recovery analysis was performed by analyzing the matrix CRM BCR 277R Estuarine Sediment and comparing the content recovered with the one certified. To determine whether the recovery significantly differed from 1, a significance test was used, and the obtained value was compared with the two-tailed critical value t_{crit} , for $n - 1$ degrees of freedom at a 95 % confidence level. All relevant calculations are summarized in Table 2.

The relative combined uncertainty was multiplied by the coverage factor $k = 2$ to obtain the expanded relative combined standard uncertainty (U) at the 95 % confidence level:

$$U = u_c * k.$$

Table 2 Relevant equations that were used for calculation of the combined relative standard uncertainties [21–23]

Equations	Explanation of parameters
$s_{xy} = \sqrt{\frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{n-2}}$	s_{xy} —residual standard deviation y_i —observed detector response $\hat{y}_i$ —predicted detector response by the regression line n —number of calibration points
$s_{x_0} = \frac{s_{xy}}{b} \sqrt{\frac{1}{N} + \frac{1}{n} + \frac{(y - \bar{y})^2}{b^2 \sum_{i=1}^n (x_i - \bar{x})^2}}$	s_{x_0} —prediction interval of the Hg mass (x) b —calibration slope N —number of parallel sample measurements x —value on the x -axis $\bar{x}$ —the mean of the x values
$u_{cal} = \frac{s_{x_0}}{c_s}$	u_{cal} —uncertainty resulting from the calibration of the instrument c_s —concentration of the sample
$\bar{R} = \frac{\bar{x}}{x_{cert}} \cdot 100$	$\bar{R}$ —mean recovery from the results of the replicate analysis of the CRM x_{cert} —certified value of the CRM used for recovery calculation $\bar{x}$ —mean of the replicates analysis of CRM
$u(\bar{R}) = \bar{R} \cdot \sqrt{\left(\frac{s_{obs}^2}{z \cdot C_{CRM}^2}\right) + \left(\frac{u(C_{CRM})}{C_{CRM}}\right)^2}$	$u(\bar{R})$ —uncertainty of the recovery s_{obs} —the standard deviation of the results from the replicate analysis of the CRM z —the number of replicates $u(C_{CRM})$ —the uncertainty of the certified value C_{CRM} —certified Hg content in the CRM C_{obs}^2 —mean value of the replicates of CRM
$t = \frac{ 1 - \bar{R} }{u(\bar{R})}$	t value for significance test
u_{RnR}	Uncertainty due to intermediate precision
$u_c = \sqrt{u_{CRM}^2 + u_{cal}^2 + u_m^2 + u_{RnR}^2 + u_R^2}$	Relative combined standard uncertainty
$u_i = \frac{u_i^2}{\sum_{i=1}^n u_i^2}$	Contribution index for each parameter that was used to calculate the combined standard uncertainty

Results and discussion

In cases of multi-point external calibration, the relationship between an analytical signal y to the analyte content x that is present in either a matrix CRM or a standard calibration solution is represented by the linear calibration function $y = a + bx$. After performing the least-squares regression (the default regression function of the instrument) on a set of calibration data, the inverse of the calibration function is used to predict the content x_0 of an unknown sample corresponding to the observed absorbance y_0 . In the case of solid sampling analysis, the calibration curve passes through the origin due to the absence of the blank sample. As there is no analyte being introduced in the combustion unit, no response of the instrument is observed, so the linear calibration function in this case can be given by $y = bx$ [24].

Despite the suggestion that matrix CRMs are intended for quality control and validation studies, many publications describe the use of CRMs for calibration purposes [14, 17, 25]. This approach is mainly suitable for techniques that require little sample preparation or decomposition, such as the one employed in the present work [24]. Due to the growth of environmental regulations and quality requirements, the demand for a CRM is increasing [26], although

the main focus is on food, water, soil, and sediment matrices [27]. Selection of a CRM either for calibration or as a tool for quality control during analysis depends on its key characteristics, such as homogeneity and stability, the chemical form of the analyte, the concentration level, the closeness of the matrix, the uncertainty associated with the analyte content, and potential interferences [15]. There is currently a lack of cement matrix CRMs, and the only available one that has a certified content of Hg (NIST CRM 633a) was proven unsuitable for calibration due to its low analyte content. Indeed, with clinker as the main ingredient of Portland cement, its Hg content is $\sim 1\text{--}5 \text{ ng g}^{-1}$ [28]. Due to the counter-current flow of materials and flue gas in colder parts of the production process (i.e., raw mill and de-dusting devices), oxidized Hg in flue gas becomes attached to particles of incoming feed, which significantly increases the concentration. Hg content of individual raw materials from the quarry and limestone varies from 7 to 47 ng g^{-1} . As the raw materials and flue gases flow in opposite direction and through different temperature gradients of the system, Hg concentration of solid material in certain parts of the process reaches up to 3400 ng g^{-1} [28]. This variable concentration requires a working range that is wide enough to cover concentrations that may be encountered during the

Table 3 Average matrix CRM masses used for calibration and their respective relative standard deviation

Matrix CRM	Average CRM mass (mg)	RSD %	Average Hg mass (ng)
ERM CC 141	12	8	1
	63.2	1	5.25
	188	2	15.6
	244	2	20.2
BCR 320R	39	0	33.2
	63.5	3	54
BCR 280R	71	3	103
	171	2	250

measurements of real samples. For this purpose, three different CRMs (ERM CC 141 Loam Soil, BCR 320R Channel Sediment, and BCR 280R Lake Sediment), which differed in analyte content, were employed for calibration. The certified values of Hg in matrix CRM are expressed in dry weight and their use in quality control should follow the recommended mass (usually 100–300 mg). But this suggestion cannot be followed when using matrix CRM for calibration, as smaller aliquots of material are needed to obtain desirable calibration points. From the Table 3, it can be seen that although for certain calibration points the recommended mass was not used, nevertheless the masses used for calibration have shown to be appropriate, because the fluctuation of the mass used is within the uncertainty of the matrix CRM which includes also the assessment of homogeneity.

Calibration is performed by weighing different masses of a CRM; therefore, another component to uncertainty is the balance used for weighing. Depending on the mass fraction of analyte of the CRM, the balance uncertainty that is used for weighing can have a significant impact on the combined uncertainty. A high analyte fraction in the matrix CRM would imply weighing small aliquots; however, in this case, the uncertainty of weighing can account for up to 10 % for masses below 0.04 mg, which is another reason why the calibration was performed with several matrix CRMs that differed in their certified Hg content.

Figure 2 shows the calibration curve and the regression coefficient that were obtained using matrix-matched CRM calibration. The certified analyte content in the matrix CRM was accompanied by the standard uncertainty, which was relatively large (Table 1), indicating that each calibration point could be within this uncertainty. Therefore, the horizontal error bars in Fig. 2 represent the uncertainty of the Hg certified content in the matrix CRM.

To estimate the uncertainty of the Hg amount in the matrix CRM and its influence on the calibration, the uncertainties of all CRMs were compared. However, when combining all the CRMs' uncertainties, the obtained combined

Fig. 2 The calibration graph that was obtained with the matrix CRM; two black arrows show two calibration points with the highest relative standard uncertainty used to construct upper and lower boundaries of the calibration curve

standard uncertainty was enormously high and did not reflect the real variability of the experimental results (the results showed much lower variations than the estimated uncertainty). Therefore, in our calculations, we only used a CRM with the highest value of standard uncertainty (ERM CC 141; 10.2 % at $k=1$). To confirm that only one value could indeed cover the uncertainties of all the matrix CRMs, we estimated both lower and upper CRM uncertainty boundaries on the calibration curve (Fig. 2). We defined these boundaries as lines connecting the origin with the minimum (maximum) value of the specific calibration points ($x \pm u$; indicated with black arrows in Fig. 2) having the highest relative uncertainty. All calibration points and their respective standard uncertainties (presented by whiskers on Fig. 2) were within these boundaries, indicating that only the CRM uncertainty with the highest value should be considered when estimating the relative combined standard uncertainty.

By contrast, spiking the matrix with a standard calibration solution is a common practice when both the samples and the calibration standards are not only in the same physical form but are also affected in the same way during analysis [16]. Because the instrumentation employed in the research was selective enough, the response of the instrument was entirely due to the presence of the Hg^{2+} , which was added through the spike. Figure 3 presents the calibration curve obtained with this approach.

In comparison to the calibration by a matrix CRM, where the uncertainty of the certified Hg content was relatively large, in this approach, even after dilution of the stock

Fig. 3 The calibration curve that was obtained by a spiked calibration

standard solution (taking into account all sources that arise during the dilution step), the uncertainty accounted for only 3 %, and it resulted from pipetting such small volumes (10–20 μL).

The linearity of both calibration curves was assessed by inspection of the distribution of the regression models' residuals, which were randomly distributed around zero. The working range for both calibration curves encompassed a mass from the LOQ to a 250-ng absolute mass of Hg. Obtaining a working range that is wide enough to prevent the need to extrapolate the calibration curve is a negative aspect of matrix CRM calibration. The possibility of extending the working range of the calibration curve that is obtained with the matrix CRM would imply utilizing other CRMs with higher Hg contents, although, again, the selection of a CRM is influenced by the closeness of the matrix to the analyzed samples. The second calibration curve also encompassed the working range from the LOQ to 250 ng Hg. However, in this case, it was easy to extend it because we were not limited by the amount of the matrix's CRM. In both calibration curves, the correlation coefficient was $R > 0.999$, which was considered satisfactory.

The conventional approach to determination of LOD as the analyte mass or concentration that corresponds to a signal three times the standard deviation of at least 10 measurements of a blank should be implemented carefully in this technique, as it is practically impossible to find such sample that is Hg-free that could be used as blank. In this case, the standard deviation of blank value measurements would be affected primarily by the baseline noise (scatter). By applying regression coefficients (although as mentioned, intercept is not applicable in this method), the obtained LOD is 1.7 ng of the absolute Hg mass and LOQ is 5.6 ng, and can be easily converted to the concentration by entering the sample mass [29]. Although the LOD was somewhat higher

Fig. 4 Relative uncertainty contribution of each source to the combined uncertainty: **a** matrix CRM calibration, **b** spiking calibration

compared to other methods for total Hg quantification [30], the obtained LOD value was suitable because raw materials used to produce cement have low Hg content [28, 31].

Combined and expanded uncertainty

From Fig. 1a, b, it is evident that the combined uncertainty depended on five main components: (1) sample mass determination u_s , (2) the uncertainty of the matrix CRM that was used for calibration/the uncertainty of the standard calibration solution $u_{\text{CRM/std}}$, (3) the uncertainty resulting from the calibration curve u_{cal} , (4) intermediate precision u_{RnR} , and (5) recovery u_R . The expanded uncertainty of the result was obtained by multiplication of u_c by the corresponding coverage factor ($k = 2$).

At the highest (> 200 ng), middle (50–150 ng), and lowest (< 50 ng) levels, $U_{\text{ex},r}$ had a value of 24.7 %, 24.9 %, and 29.2 %, respectively, for calibration with the matrix CRM. The spiked calibration approach had lower uncertainties, at 15 %, 15.5 %, and 21.7 %, respectively. The comparison of relative contributors to the combined uncertainty using both calibration approaches can be seen in Fig. 4.

Table 4 Hg concentration in selected samples from cement production determined using both calibration approaches

Sample code	Matrix CRM calibration $c \pm u$ (ng g ⁻¹)	Spike calibration
Limestone	14.1 ± 4.1	13.8 ± 3
Limestone	52.9 ± 13.2	51 ± 7.9
Limestone	36.9 ± 9.2	34.9 ± 5.4
Raw meal (preheater)	32.6 ± 9.5	30.2 ± 6.6
Raw meal (preheater)	17.7 ± 5.2	16.4 ± 3.6
Raw meal (preheater)	4.14 ± 1.3	3.83 ± 0.83
Raw meal (preheater)	2.57 ± 0.75	2.38 ± 0.5
Raw meal (preheater)	4.78 ± 1.4	4.43 ± 0.96
Raw meal (preheater)	154 ± 38.3	142 ± 22
Raw meal (preheater)	164 ± 40.8	152 ± 23.6
Filter bag dust	2448 ± 604	2265 ± 340
Filter bag dust	525 ± 129	485 ± 72.8

Fig. 5 Comparison of the total Hg in samples that were obtained with two calibration approaches and their respective uncertainties

The biggest contributor to the combined uncertainty in the measurements that were performed with the matrix CRM calibration was the Hg mass fraction of the CRM itself at all concentration levels, with the uncertainty increasing with the concentration. The same was also observed in the spiked calibration approach, although the relative contribution was significantly lower. The relative standard uncertainty that resulted from the calibration curve was the same for both approaches, although its contribution was more pronounced in the lower range of the spiked calibration. The highest contribution in the spiked calibration came from the u_R , which stemmed from the uncertainty of the BCR 277R itself. The contribution of u_{RnR} was relatively small and mostly dependent on the concentration level. The sample mass determination had a negligible contribution to the overall uncertainty.

The comparison of the results and the corresponding uncertainties (in logarithmic scale) of the real samples (limestone, raw meal, filter dust, clinker; Table 4) that were obtained with the methodology that was employed in this study are presented in Fig. 5. The results are obtained by measuring Hg content using both calibration approaches.

Method A (x axis) represents the results that were obtained with the matrix CRM calibration approach, while method B (y axis) shows the results that were obtained with a spiked calibration. The whiskers represent the corresponding uncertainties of the methods. The obtained slope of 0.939 shows good agreement between the results that were obtained with both approaches; slight differences can be observed in the samples with a higher concentration.

Certainty, there is a slight difference in the slopes obtained with both calibration approaches. The difference could be due to different matrix CRM used to construct the calibration curve, as in this case we have used three matrix CRM. Another issue could be attributed to the uncertainty of the matrix CRM, meaning that when the calibration curve is constructed, it is done without considering this very important information. Even though the calibration curve covers all points, the residual standard deviation (s_{xy}) of the regression in the case of matrix CRM calibration is higher (838) than in the spike calibration (723).

Metrological traceability The purpose of a method validation is to confirm that the method employed is suitable for its intended use, and when it is correctly applied, produces reliable results and confirms the effectiveness of the analytical method with a high degree of accuracy. Together with the measurement uncertainty and metrological traceability, they present the key concepts in the measurement science. The calibration of the instrumentation used in the study was based on the specified property value that is traceable to the SI quantities which serves to link the results to the SI units.

Conclusions

The quantification of the total Hg by direct thermal decomposition AAS has been shown to be suitable for solid samples from cement production. Although both matrix-matched CRM and the spike calibration can be utilized for calibration of the instrumentation employed in the study, the need for several matrix CRMs that differ in Hg content and the uncertainty of the mass fraction are the main drawbacks when choosing to calibrate the instrument with matrix CRM. From all possible alternatives to calibrate the instrument, adding standard calibration solutions to the solid matrix showed to be a convenient calibration approach because the uncertainty of the standard calibration solution is smaller compared to the matrix-matched CRM. The standard addition method would be suitable approach in order to investigate the matrix

effect, but this would produce much higher uncertainty on top of the existing one of the natural Hg. Even though the matrix is subjected to the change after the combustion in the second approach to calibration, it did not affect the quantitative release of the added Hg. By introducing the optimal mass of the sample in the combustion unit (0.1 g in our case), the issue of homogeneity of the analyzed sample can be overcome. The obtained LOD was acceptable for the raw materials that are used for cement production. The expanded uncertainty in the lower concentration range, where most of the materials are expected to lie, was 21.6 %, which can be considered acceptable.

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