ГОДИШНИК НА УНИВЕРСИТЕТА ПО АРХИТЕКТУРА, СТРОИТЕЛСТВО И ГЕОДЕЗИЯ
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MICROWAVE-ASSISTED DIGESTION OF SEWAGE SLUDGE MATERIALS FOR THE DETERMINATION OF CADMIUM USING ETAAS

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Keywords: *sewage sludge, Cd, CRM, validation, uncertainty estimation*

ABSTRACT

A simple method for the determination of total cadmium content in sewage sludge materials, based on microwave assisted digestion of 0,1 g of sample with 10 mL diluted acid mixture, containing 20% v/v nitric acid and 5% v/v hydrofluoric acid in combination with microwave heating (up to 240 °C) at high pressure (up to 150 bar) is presented. The resultant clear solutions are analysed for Cd using electrothermal atomic absorption spectrometry. The optimum instrument parameters are presented. The method is validated and method performance parameters have been established. It was successfully used for analysis of certified reference materials and in interlaboratory comparison proficiency testing scheme.

1. Introduction

The council directive 86/278/EEC on the protection of the environment when sewage sludge is used in agriculture regulates the use of sewage sludge in such a way as to prevent harmful effects on soil, vegetables, animals and man. Limit values for concentrations of Cd, Cu, Hg, Ni, Pb and Zn in soil and sewage sludge are established, as well as parameters of the sludge to be analysed [1]. The common approach for sewage sludge sample digestion employs the use of concentrated acids [2 – 5], sequential extraction procedure [6], aqua regia extraction [7, 8] and in very limited cases – diluted acid mixtures [9]. This paper presents a method based

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on the concept of using diluted acids for sample digestion [10]. The feasibility of the use of diluted acid solutions for sample treatment originates both from the high pressure and high temperatures reached in the closed vessels. Higher temperatures cause more complete destruction of the sample matrix and improve method accuracy [11]. Diluted nitric acid solutions have been successfully used in microwave-assisted plant digestion [12 – 14] and sewage sludge heavy metal removal [16], generating low blank levels and low relative standard deviations. Compared to concentrated acid mixtures, diluted acids generate fewer residues and do not require high dilution factors prior to analyte measurements, making the analysis easier, faster and cheaper, according to the green chemistry trends [10].

2. Materials and Methods

Reagents

Cadmium stock solution – 1000 mg/mL, Merck, Darmstadt, Gemany (or equivalent);

Concentrated HNO_3 – ~65% (Merck, Darmstadt, Gemany);

Concentrated HF – ~40% (Merck, Darmstadt, Gemany);

Palladium Matrix Modifier (Flucka);

H_2O – 18,2 mΩ/cm, MilliQ-system, Milipore, MD.

Sample Preparation

A 10 mL mixture of 20% v/v of nitric acid and 5% v/v hydrofluoric acid is added to about 0,10 g sub-sample of the sewage sludge certified reference material BCR 144R (Institute for Reference Materials and Measurements, IRMM) with certified value for total Cd content of 1,82±0,14 mg/kg using analytical microbalance (Mettler Toledo AX504 with accuracy of 0,0001 g). The vessels with the samples are then placed into a microwave reactor of the microwave UltraCLAVE (Milestone, US). The reaction vessels were pressurized to 45 bar with nitrogen gas. The microwave program is presented in Table 1. The maximum applied power for all steps is 1000 W, and is limited by the set maximum temperatures and pressures.

Table 1. Temperature programme for microwave assisted digestion of sewage sludge materials

Step	Time, min	Temperature inside the vessels, °C	Temperature in the external jacket, °C	Pressure, bar
1	45	120	50	100
2	15	240	50	150
3	30	240	50	150

ETAAS Measurement

Measurements for Cd in the sewage sludge material were performed on Zeeman Atomic Absorption Spectrometer ZEEnit 650 (Analytik Jena). Hollow-cathode lamp for Cd was used as light source. Optimal temperature programme includes sample pyrolysis temperature of 500 °C and atomization temperature of 1500 °C with prolonged hold-times of 20 s and 4 s, respectively. Peak area is used for quantification.

Table 2. Optimum temperature programme for ETAAS determination of Cd in sewage sludge materials

Drying 1	
Temperature, °C	80
Ramp, °C/s	5
Hold time, s	20
Drying 2	
Temperature, °C	95
Ramp, °C/s	2
Hold time, s	20
Drying 3	
Temperature, °C	110
Ramp, °C/s	2
Hold time, s	20
Pyrolysis	
Temperature, °C	500
Ramp, °C/s	250
Hold time, s	20
Atomization	
Temperature, °C	1500
Ramp, °C/s	Full Power
Hold time, s	4
Cleaning	
Temperature, °C	2300
Ramp, °C/s	2300
Hold time, s	4

Method validation

According to ISO 17025 [16], validation is the confirmation by examination and the provision of objective evidence that the particular requirements for a specific intended use are fulfilled. It requires that the laboratory validates non-standard methods, laboratory-developed methods, standard methods used outside their intended scope, and modified of standard methods to confirm that they are fit for their intended use. Extensive validation is necessary to establish that the method of choice is under statistical control each time the method is used, so it fully meets the needs of the intended application. Targeted method performance criteria for the determination of Cd in sewage sludge materials were the following:

- Calibration curve: a coefficient of determination (R^2) of at least 0,995 using a linear curve. A set of four standard solution prepared freshly on every measurement day with Cd concentrations of 0,5 μg/L, 1,0 μg/L, 1,5 μg/L and 2,0 μg/L were used for construction of the calibration curves. Linearity was determined via repeated measurements of the standard solutions.
- Maximum allowed RSD on replicates (not for blanks): less than 5%.
- Maximum and minimum allowed blank levels: between -0,05 μg/L and 0,05 μg/L.

- Instrumental Limit of Detection (LOD) and Limit of Quantitation (LOQ): LOD < 0,1 μg/L; LOQ < 0,4 μg/L. LOD/LOQ were determined via the standard deviations of method blanks. Minimum and maximum allowed blank levels were established in the same experiments.
- Working range: between 0,5 and 2,0 μg/L for the calibration solutions.
- Repeatability (standard deviation): less than 10% – Repeatability and intermediate precision were determined by replicate analysis of a CRM and assessment of between-day effects.
- Trueness – to be able to measure the certified value of a CRM within combined uncertainty. Trueness, accuracy and method bias were checked against the certified value of the total Cd content in the BCR 144R.
- Relative combined uncertainty – maximum 10%.

Uncertainty estimation

The experimental design according to ISO 21748 [17] was set up in a way so that the repeatability, reproducibility and trueness estimates are used for measurement uncertainty estimation. Details on calculations are described elsewhere [18, 19]. Trueness was proven by measurement of three independent samples of a CRM on two different days. From these data the uncertainty of trueness and method bias were calculated. Repeatability and intermediate precision were determined by replicate analysis and assessment of between-day effects. This was achieved by preparation of three independent samples of a CRM on three extra days. Combination from these data and the data obtained for trueness were used for calculation of the uncertainties of repeatability and due to intermediate precision. Measurement uncertainty components of repeatability and due to intermediate precision can easily be calculated using the ANOVA function in the Microsoft Excel.

3. Results and Discussion

The electrothermal atomic absorption spectrometry (ETAAS) is a single-element method that is based on the capability of a free, ground state atom to absorb very specific wavelengths of light. In case of complex matrices background absorption may occur. In order to avoid that problem Zeeman background correction is applied. Therefore, no specific measurements have been performed.

A calibration line between 0,5 and 2,0 μg/L was constructed using dilution of a stock Cd solution. The calibration returned a coefficient of determination of 0,9996, which meets the set criteria. The plot of the residuals shows curvature typically seen for ETAAS measurement, even in a narrow range of concentrations. However, as the residuals were of the same magnitude as the measurement RSD (maximum 2,1%), and the coefficient of determination exceeded the set criteria, a linear calibration function was considered to be suitable. The RSDs of the results for the lowest and highest standard are sufficiently similar to allow the use of relative uncertainty over the whole calibration range.

Maximum and minimum allowed levels of the element concentrations in the blank solutions are defined to check for contamination of the samples or the calibration standards. Considering the combined uncertainty of the method, the absolute value of blank levels must be less than 10% of the concentration of the lowest standard to ensure that blanks do not significantly alter the measurement uncertainty. The results are presented in Table 3. The lowest standard in the calibration curve is 0,5 μg/L. Based on the results obtained for the

method blanks, the criteria for Cd is met. Therefore the minimum and maximum allowed blanks should be ±10% of the concentration of the lowest standard.

Table 3. Measurement of Cd concentration in blank solutions with ETAAS

Blank 1	-0,0321 µg/L
Blank 2	-0,0261 µg/L
Blank 3	-0,0192 µg/L
Blank 4	-0,0163 µg/L
Blank 5	0,0147 µg/L
Blank 6	-0,0348 µg/L
Blank 7	-0,0340 µg/L
Blank 8	-0,0313 µg/L
Blank 9	-0,0432 µg/L
Blank 10	-0,0337 µg/L
Mean	***-0,0256* µg/L**
Targeted value (±10% of the lowest standard)	±0,05 µg/L

As it was not possible to find commercially available sewage sludge reference materials with blank levels of Cd, the standard deviation (s) of repeat measurements of method blanks were used for the estimation of the LOD $\left(3s\sqrt{2}\right)$ and LOQ $\left(10s\sqrt{2}\right)$. These were prepared using sample digestion reagents that were treated in the same way as samples. A total of 10 method blanks were measured. Calculations show LOD = 0,07 µg/L and LOQ = 0,23 µg/L. The LOQ is well below the concentration of the lowest standard (0,5 µg/L). Only samples above the concentration of the lowest standard will be measured. To calculate the LOQ in the sample, the LOQ in solution was multiplied by 10 and divided by 0,1 (i.e. the typical dilution of a sample). Experiments show that when measuring the Cd content in BCR 144R, the sample had to be further diluted 1:10 in order concentration of Cd to fall into the defined working range. In all cases the values obtained were compared to the certified values. No significant bias was found.

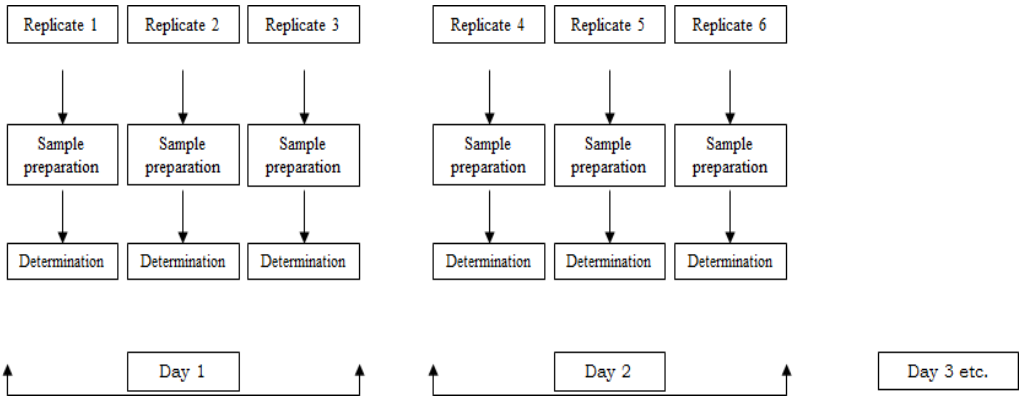

Figure 1. Trueness, repeatability and intermediate precision experiments set up

For the estimation of trueness, accuracy and method bias, as well as the repeatability and intermediate precision, three independent samples of BCR-144R were prepared on two different days and measured for Cd content. From these data the trueness and bias were calculated. Three independent samples were prepared on three extra days. From these data repeatability and intermediate precision were calculated (Fig. 1).

Total of 6 sub-samples the CRM have been measured on two different days to incorporate the reproducibility in the trueness check. The results for Cd showed no bias for BCR 144R. The uncertainty of trueness for Cd was calculated and the result is presented in Table 4. Additionally, 3 sub-samples of the CRM were measured on 3 extra days (5 different days, using 5 different calibration curves in total). The results were used to calculate the repeatability for Cd (5,1%). The uncertainties due to repeatability and intermediate precision, calculated based on ANOVA-single factor calculation, are expressed as relative uncertainties and presented in Table 4.

Table 4. Calculation of expanded measurement uncertainty

Uncertainty due to repeatability	**Uncertainty due to day-to-day variation**	**Uncertainty of trueness**		**Relative, expanded, uncertainty**
$u_{r,rel}$, %	$u_{ip,rel}$, %	$u_{t,rel}$, %		U_{rel}, %
5,1	0,6	2,6	$k = 2$	**12**

A comparison between the targets of the method performance criteria and validation results is presented in Table 5.

Table 5. Targeted and achieved method performance criteria for the microwave assisted digestion and determination of Cd in sewage sludge CRM using ETAAS

Criteria	**Target**	**Achieved/Proven**
$\underline{R}^2$ between 0,5 and 2,0 µg/L	> 0,995	0,9996
LOD	< 0,1 µg/L	0,07 µg/L
LOQ	< 0,4 µg/L	0,23 µg/L
Working range between	0,5 and 2,0 µg/L	0,5 – 2,0 µg/L
Repeatability	less than 10%	5,1%
Reproducibility	less than 10%	0,6%
Maximum allowed RSD on replicates	less than 5%	less than 5%
Maximum allowed blank levels	less than 0,05 µg/L	0,05 µg/L
Minimum allowed blank levels	more than -0,05 µg/L	-0,05 µg/L
Trueness	CRM within combined uncertainty	Yes
Relative combined uncertainty	maximum 10 %	6%

4. Conclusion

The method for the determination of Cd in sewage sludge materials using microwave-assisted dilute acid digestion and subsequent ETAAS determination is considered fit for its

intended purpose. Method validation experiments returned results within the targeted method performance criteria, which confirm that the method is under statistical control. In addition, the method was also tested by participation in a proficiency testing scheme (QualityConsult 08SS1, total element contents in sewage sludge). This scheme involves interlaboratory comparison in which consensus values of the determined parameters are assigned to the tested material. Normally acceptable Z-scores are considered between -2,0 and 2,0. Within the 08SS1 exercise, a satisfactory Z-score was achieved for Cd (-1,0) with an intercomparison median concentration of 5,70 mg/kg of Cd in the sewage sludge material measured.

The validity of the method for the microwave-assisted digestion using diluted acids is further assessed within the laboratory inter-comparison, organised by the IRMM in the frame of the characterisation study of ERM-CC144 [20].

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МИКРОВЪЛНОВО РАЗЛАГАНЕ НА УТАЙКИ ЗА ОПРЕДЕЛЯНЕ НА КАДМИЙ ЧРЕЗ ЕЛЕКТРОТЕРМИЧНА АТОМНОАБСОРБЦИОННА СПЕКТРОМЕТРИЯ

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Ключови думи: *утайки, кадмий, СРМ, валидиране, оценка на неопределеността*

РЕЗЮМЕ

Представен е метод за определяне на кадмий в утайки, основаващ се на разлагането на 0,1 g проба с 10 mL разредена киселинна смес, съдържаща 20% азотна киселина и 5% флуороводородна киселина, в комбинация с микровълново нагряване (до 240 °C) при високо налягане (до 150 bar) според дефинирана температурна програма. Концентрацията на кадмий в разложените проби е определена чрез електротермична атомноабсорбционна спектрометрия. Представена е оптималната температурна програма. Методът е валидиран и са определени неговите характеристики. Той е успешно приложен при анализ на сертифицирани сравнителни материали и в междулабораторно сравнение при изпитване на пригодност.

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