INVESTIGATING ON CONDITIONS OF WASTEWATER AND SEDIMENT SAMPLE PREPARATIONS FOR SELENIUM DETERMINATION USING HG-AAS

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ABSTRACT

Analysis of selenium (Se) in environmental sample matrices is often limited due to equipment sensitivity, analytic loss, and contamination during sample preparation and storage. The present study aimed to complete a reliable routine analytical procedure for determining total selenium contents in wastewater and sediment using hydride generation atomic absorption spectrometry. Different wet digestions were investigated for sample preparation. The mixture of HNO_3:H_2SO_4 acids (*10:1 = v:v*) treated the wastewater matrix effectively, while the complete decomposition of sediment, more complex matrices, was achieved by HNO_3:H_2SO_4:$HClO_4$ (*10:1:2 = v:v:v*). The method detection and quantification limits (MDL-MQL) were 0.088 - 0.29 µg L^{-1} for wastewater and 13.6 – 45.2 µg kg^{-1} for sediment, respectively. The recoveries reached over 95% for both sample matrices, even sediment with total organic carbon (TOC) up to 180 mg g^{-1}. Repeatability and reproducibility were favorable according to the requirements presented in Appendix F of AOAC (2016) for analytical method validation. Consequently, the proposed method can be further applied for environmental monitoring and management purposes.

KHẢO SÁT ĐIỀU KIỆN XỬ LÝ MẪU NƯỚC THẢI VÀ TRẦM TÍCH ĐỂ XÁC ĐỊNH HÀM LƯỢNG SELEN BẰNG PHƯƠNG PHÁP HG-AAS

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TỪ KHÓA

Selen
Nguyên tố thiết yếu
Bùn lắng
Quan trắc môi trường
Rủi ro sức khỏe

TÓM TẮT

Phân tích selen (Se) trong các mẫu môi trường thường bị hạn chế do độ nhạy của thiết bị, mất và nhiễm bẩn chất phân tích trong quá trình xử lý và bảo quản mẫu. Mục đích của nghiên cứu này là hoàn thiện quy trình phân tích thường quy tin cậy để xác định tổng hàm lượng selen trong nước thải và trầm tích bằng kỹ thuật hóa hơi hydrua kết nối phổ hấp thu nguyên tử. Các quy trình phân hủy mẫu ướt khác nhau được khảo sát cho xử lý mẫu. Hỗn hợp HNO_3:H_2SO_4 (*10:1 = v:v)* xử lý hiệu quả nền mẫu nước, trong khi đó, quá trình phân hủy hoàn toàn trầm tích, với thành phần nền phức tạp hơn, đạt được với HNO_3:H_2SO_4:$HClO_4$ (*10:1:2 = v:v:v*). Giới hạn phát hiện và định lượng của phương pháp phân tích (MDL – MQL) lần lượt là 0,088 – 0,29 µg L^{-1} cho nước thải và 13,6 – 45,2 µg kg^{-1} cho trầm tích. Hiệu suất thu hồi đạt trên 95% cho cả hai nền mẫu, bất kể trầm tích có hàm lượng tổng carbon hữu cơ lên đến 180 mg g^{-1}. Độ lặp lại và tái lập đáp ứng theo phụ lục F của AOAC (2016) dùng cho thẩm định phương pháp phân tích. Do đó, phương pháp được đề xuất có thể được áp dụng phục vụ mục đích quan trắc và quản lý môi trường.

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1. Introduction

Selenium (Se) is a metalloid distributed widely in soil, water, and air, and exists in many different oxidation states in nature, most commonly -2, 0, +4, +6 [1], [2]. Natural weathering processes, i.e., geothermal, volcanic activity, water intrusion into rocks [3], [4] and anthropogenic activities, i.e., materials industry, electronics, agricultural production, and medicine, are considered sources of Se emissions into the environment [4], [5]. Se content is about 1– 5000 nmol L^{-1} in water, and selenite is the predominant form in reducing conditions and is pH-dependent (H_2SeO_3, $HSeO_3^-$, SeO_3^-, $HSe_2O_5^-$, and $Se_2O_5^{2-}$) [6]. Meanwhile, selenate predominates in oxidizing conditions and exists mainly as SeO_4^{2-}. Selenium speciation binds to suspended particulate matter such as iron oxides or clay minerals that are deposited to form sludge and sediments. Selenium is accumulated in aquatic plants and animals through free ion forms in water and food chains. In sludge, the forms of dimethyl selenide $(CH_3)_2Se$, dimethyl diselenide $(CH_3)_2Se_2$, and dimethylselenon $(CH_3)_2SeO_2$ are the predominant forms. In aquatic plants, these compounds are metabolized from selenomethionine, selenocysteine, and selenoprotein. Besides, selenium also binds with other metals forming compounds such as CuSe, PbSe, and ZnSe [1]. Overall, selenium compositions are important for human and animal health. Selenium, at a small level, participates in the processes of vision regulation for the human body. In addition, Selenium compounds can increase immunity, anti-oxidation and slow down the aging processes. Lack of selenium could lead to cardiovascular problems, lowered immunity, and increased risk of infections. However, consuming too much Se can negatively affect health through symptoms of loss of appetite, malnutrition, damaged teeth, fingernails, and toenails [7].

Sample preparation is known as an important process for the accuracy of Se analysis. The dry and wet digestion techniques have been reported for various sample matrices, e.g., sludge, sediment, water, etc., to determine Se content. Among them, dry digestion often obtains good performance, even with high organic content in the sample matrix, and can be applied to many different sample types; however, the high temperature of dry digestion can cause Se loss during treatment. Meanwhile, the wet method exhibits the advantage of dissolving and completely oxidizing the matrix at a lower temperature than the dry one. Strong acids such as nitric (HNO_3), hydrochloric (HCl), sulfuric (H_2SO_4), and perchloric ($HClO_4$) acids are commonly employed [8]. Currently, the sample preparation containing selenium, after being digested with a strong acid mixture, can be determined using various equipment, e.g., ICP-OES [9], ICP-MS [10], atomic fluorescence (AFS) [11], atomic absorption spectrometry with atomization techniques such as flame (F-AAS), graphite furnace (GF-AAS), and hydride generation (HG-AAS) [11], [12]. Because of the low concentration in biological and environmental samples characterized by complex matrix, it is necessary to use sample preparation procedures and suitable analytical techniques for Se quantification [13]. The methods of ICP-MS and GF-AAS, even with high sensitivity for Se analysis, are significantly affected by the matrix components [14] - [17]. FAAS is less sensitive to detect Se in environmental samples. In contrast, HG-AAS is proven to overcome the above disadvantages based on the characteristics of selenium being separated from the sample matrix, thereby reducing the influence of the matrix component on the analytical method, and the method detection limit can reach at μg L^{-1} level. Nevertheless, selenium analysis on HG-AAS requires that selenium exists as Se^{IV} for forming hydride vapor, i.e., SeH_2 [13]. Consequently, selenium species in the sample matrix must be completely converted into free Se^{IV}. Unfortunately, selenium loss and contamination can occur during sample preparation and storage. Se^{IV} in the sample and standard solutions can be oxidized to Se^{VI} during storage before analysis. Therefore, the objectives of the present study were to complete a reliable routine procedure to analyze Se in wastewater and sediment with high sensitivity, stability, and accuracy using HG-AAS. To reach the aims, experiments using different acid mixtures were investigated

for the digestion of wastewater and sediment samples. The effect of acid concentration on the production of selenium hydride vapor and its stability over time was performed.

2. Methodology

2.1. Chemicals and apparatus

All chemicals were purchased from Merck, including 37% (*w/v*) HCl, 65% (*w/v*) HNO_3, 98% (*w/v*) H_2SO_4, 72% (*w/v*) $HClO_4$, solid NaOH, $NaBH_4$, a selenium standard stock solution of 1000 mg L^{-1} Se^{VI}. Perkin Elmer AAS 603 was used for selenium analysis.

The standard solution of 50 mg L^{-1} Se^{VI} was prepared monthly from 1000 mg L^{-1} stock standard solution by diluting with 6M HCl. This standard solution was used to prepare working standard solutions for daily analysis.

2.2. Investigation of hydride generation and stability of selenium working standard

The operating parameters of the HG-AAS system are shown in Table 1. The equipment was conducted when a sample solution, 0.22% $NaBH_4$ in 0.05 % NaOH and HCl, was mixed by a three-channel peristaltic pump. Experiments were performed to investigate the influence of reaction conditions on the hydride-forming efficiency. The standard solution was prepared in 1M HCl. The hydride generation was studied using different acid concentrations, varying from 1M, 3M, and 6M, respectively. The same experiments in selected sample matrix were deployed with 3M and 6M acid concentrations. It was noted that the HCl concentration in the reaction coil depended on the sample aspiration rate, and the acid/ base concentrations in the three channels. The tests to evaluate the stability of the Se^{IV} working standard solution were prepared in HCl with different concentrations daily. The experiments were investigated at three different concentrations of Se^{IV}, including 1 µg L^{-1}, 4 µg L^{-1}, and 10 µg L^{-1}. The solutions were mixed in HCl 1M, 3M, and 6M HCl for each concentration, respectively.

Table 1. *Operation parameters on the HG-AAS system*

Element	Selenium
Hollow cathode lamp current	10 mA
Argon flow rate	25- 30 mL min^{-1}
Atomization temperature	900 ^{0}C
Wavelength	196.1 nm
Slit width	2 nm
Reducing reagent	0.22% $NaBH_4$ in 0.05 % NaOH

2.3. Chemical selection for sample preparation

2.3.1. Wastewater matrix

Wastewater samples for the study were collected at low tide from the drainage creek of the Binh Dien wholesale market, characterized by agricultural, aquacultural, and seafood products in District 8, Ho Chi Minh City. Four procedures of sample preparation based on the wet digestion method were performed. The acid mixtures were used, including W-1: 5 mL of 65% HNO_3; W-2: 5 mL of 65% HNO_3 + 0.5 mL of 98% H_2SO_4; W-3: 5 mL of 65% HNO_3 + 0.5 mL of 98% H_2SO_4 + 1 mL of 70% $HClO_4$; W-4: 3 mL of 65% HNO_3 + 9 mL of 37% HCl. The digestions were performed on an open system using glass conical flasks of 250 mL with the lid of the glass dishes and the sand-combined pots. Briefly, 50 mL of wastewater was taken into a conical flask with an acid mixture. The sample was heated at approximately 110 °C for 2 hours and then gradually increased to 300 ^{o}C for at least 1 hour until transparent and 1 mL remained. The sample was transferred to a 40 mL glass vial containing 30 mL of 6M HCl acid, which was heated in a water bath at 90 ^{o}C for 1 hour, then filled to the 40 mL volume using distilled water. The selenium analysis was performed on AAS 603 by recording the absorbance signal at 196 nm. The efficiency of the acid digestion was calculated based on the recovery of spiked samples.

2.3.2. Sediment matrix

Sediment was collected at the same sampling site with wastewater. Three sample preparations were performed with mixtures of strong acids, i.e., including S-1: 10 mL of 65% HNO_3 + 1 mL of 98%H_2SO_4 + 2 mL of 70% $HClO_4$; S-2: 10 mL of 65% HNO_3 + 1 mL of 98% H_2SO_4 + 4 mL of 70% $HClO_4$; S-3: 3 mL of 65% HNO_3 + 9 mL of 37% HCl. The same open system and temperature program for wastewater sample preparation were applied for sediment. Briefly, 1 g of the sediment was weighed into a glass conical flask of 250 mL with an investigated acid mixture. The samples were digested until completely white. The sample was filled using distilled water and centrifuged to remove the residue. The solution was taken into a 40 mL glass vial containing 30 mL of 6M HCl acid, heated in a water bath at 90 ^oC for 1 hour, then filled and measured selenium content using AAS 603. To measure recovery efficiency, the Se standard solution was spiked to the investigated sediment sample with the high TOC content, which was mixed using a vortex and let to equilibrate within 24 hours before conducting selenium analysis.

2.4. Analytical method evaluation

A calibration curve was conducted from Se^{IV} standard solutions with concentrations of 0.5, 1.0, 2.0, 4.0, 6.0, 8.0, and 10 µg L^{-1} which were stored in 3M HCl and used during the day. The calibration curve was based on a relationship between the Se concentrations (x) and their corresponding absorbance values (y) measured at 196 nm as follows y = *a*x + b. The detection and quantification limits (MDL and MQL) for wastewater and sediment were estimated by analyzing 11 blank samples (only containing digestion reagents with the optimized digestion procedure, respectively).

$$MDL = \frac{3{,}9 \times SD}{a} \quad (1)$$

$$MQL = 3.3 \times MDL \quad (2)$$

a: the slope of the calibration curve

SD: the standard deviation values calculated from 11 blank samples

Repeatability and reproducibility were evaluated using the data from four experiments on four different days. The results were assessed through the Horowitz formula (equation 3).

$$S_{r_{max,r\%}} = 0.67 \times 2^{0.5(1-\log C)} \quad (3)$$

$S_{r_{max,r\%}}$ *is the allowable relative standard deviation for repeatability*

C is the concentration of the analyte

Certified reference material (CRM)/ Mess-3 was used to ensure the overall method accuracy. Six samples were performed repeatable using the optimized sample preparation procedure. Selenium content (average $\pm$ SD), recovery (equation 4), and relative standard deviation (RSD by a ratio of SD to average/mean content, calculated in percentage) were determined. The student Test (equation 5) was used to compare the measured result and certified value.

$$H(\%) = \frac{C - C_{Spiked}}{C_{sample}} * 100 \quad (4)$$

C: total analyte content calculated from calculations curve

C_{spiked}*: analyte content spiked into the initial sample*

$C_{sample:}$ *mean content of analyte measured in the initial sample*

$$t_{TN} = \frac{|x_{det} - x_{CRM}|}{\sqrt{u_{det}^2 + u_{CRM}^2}} \sqrt{n} \quad (5)$$

x_{det}: *measured value of the analyte*

x_{CRM}: *certified value of the analyte*

u^2 : *variance of analysis*

3. Results and discussion

3.1. Effects of reaction conditions and storage on selenium analysis

HCl concentration is important in generating hydride vapor because if the acid concentration is low, the hydride generation ability will be reduced, reducing sensitivity. However, if the acid concentration is too high, it will reduce the life of machinery and lines of peristaltic pumps, waste a lot of chemicals, and be uneconomical. On the other hand, it also affects the durability of Se^{IV} during storage. The influence of HCl concentration on hydride forming is shown in Figure 1. The absorbance signal increased while the acid concentration increased and gradually stabilized at the acid concentration greater than 3M. It could be explained by a part of H^+ always reacting with BH_4^- to form newborn H^* which converts right into H_2 during mixing (equation 6), which decreases the remaining H^+ to form hydride (equation 7). In contrast, at higher HCl concentrations, the formation of H_2 contributes to the liquid-air separation for carrying the hydride (SeH_2) to the atomizer cell. Consequently, 3M HCl was chosen to prepare samples for further analysis.

$$BH_4^- + 3H_2O + H^+ \rightarrow H_3BO_3 + 8H^* \quad (6)$$

$$4H_2SeO_3 + 3BH_4^- + 3H^+ \rightarrow 3H_3BO_3 + 3H_2O + 4SeH_2 \quad (7)$$

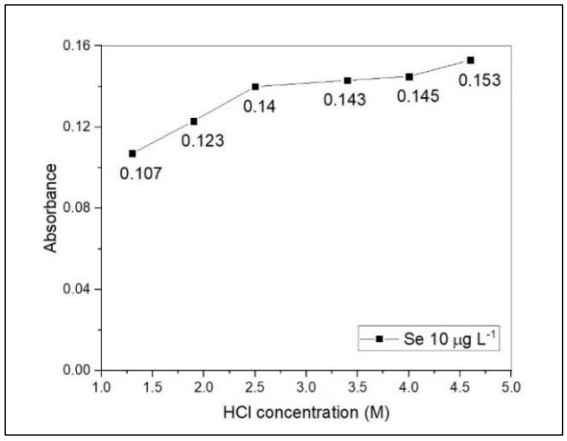
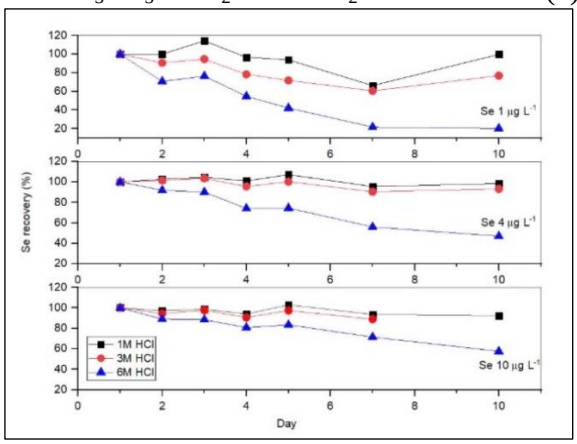


Figure 1. *Influence of HCl concentration on hydride generation. (10 µg L^{-1} Se^{IV}; reaction conditions: 1M, 3M, and 6M HCl, respectively; 0.22% $NaBH_4$ in 0.05 % NaOH)*



Figures 2. *Se^{IV} stability over 10 days of storage (Se^{IV} prepared in different concentrations of 1, 4, and 10 µg L^{-1}; reaction conditions: 1M, 3M, and 6M HCl, respectively; 0.22% NaBH4 in 0.05 % NaOH)*

The stability of the different standard solutions (Se^{IV}) during 10 days of storage is presented in Figure 2. The Se recovery prepared at 6M HCl decreased significantly daily. We suggest the reason is due to the high HCl concentration that leads to a significant amount of Cl_2 being simultaneously produced in reducing Se^{VI} to Se^{IV}. In addition, during storage, O_2 could penetrate the solution, which oxidizes Cl^- to Cl_2 [18], and Se^{IV} is back converted into Se^{VI} (equation 8), i.e., loss of Se^{IV} during storage.

$$3H^+ + HSeO_4^- + 2Cl^- \leftrightarrow H_2SeO_3 + H_2O + Cl_2 \quad (8)$$

3.2. Performance of analytical methods for selenium analysis in wastewater

To evaluate the efficiency of acid digestion and the effects of the sample matrix, the wastewater sample was spiked at a concentration of Se^{IV} 4 µg L^{-1}. The four procedures of sample preparation based on W-1, W-2, W-3, and W-4 (n = 5 for each) were performed for selenium recovery calculation. The results show that the selenium recovery was less than 80%, and the deviation was large while applying the sample preparation with HNO_3 (W-1). The combination of strong acid mixtures, i.e., W-2, W-3, and W-4 procedures, increased recoveries by more than

95% and high stability, i.e., SD < 5% (Figure 3). The performance of HNO_3 was not enough to decompose the sample matrix completely. Moreover, the remaining organic substances could reduce Se^{VI} to Se^{IV}, causing sample loss during digestion. In contrast, the performance of the W-2 procedure increased selenium recovery due to increased reaction temperature using H_2SO_4. W-3 and W-4 increased sample digestibility, which could be attributed to the combination of $HClO_4$ and HCl in a strongly oxidizing condition inducing the selenium forms as Se^{VI}, a non-volatile compound. Thus, the sample preparation using HNO_3:H_2SO_4 (W-2), HNO_3:H_2SO_4:$HClO_4$ (W-3), and HNO_3:HCl (W-4) worked well on the investigated samples. However, based on cost, simplicity, and execution time criteria. The mixture of the HNO_3:H_2SO_4 (W-2) was selected for further application.

The standard deviation of 11 blank samples was measured using the W-2 procedure. The absorbance values of 11 blank samples were as follows: 0.00632, 0.00628, 0.00663, 0.00690, 0.00692, 0.00680, 0.00709, 0.00630, 0.00647, 0.00661, 0.00622. MDL and MQL were calculated based on the calibration curve (y = 0.0134x + 0.0008) with values of 0.088 µg L^{-1} and 0.29 µg L^{-1}, respectively. The results demonstrated a favorable method of recovery and repeatability according to Appendix F of AOAC (2016), which can be applied to selenium analysis with low concentration in wastewater samples.

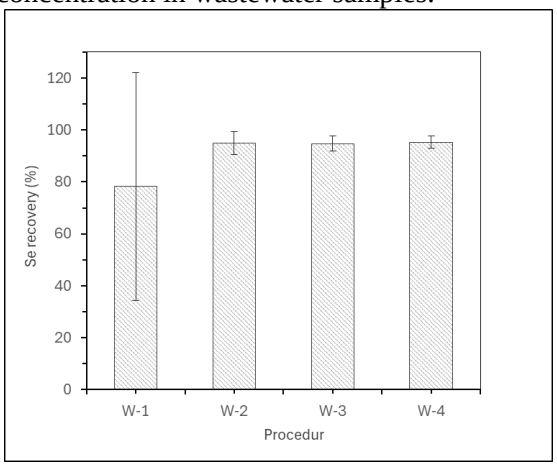


Figure 3. *Efficiency of different procedures for the water sample preparation (V_{sample}: 50 mL; 4 µg L^{-1} spiked Se^{IV} (n = 5); W-1: 5 mL HNO_3; W-2: 5 mL HNO_3 + 0.5 mL H_2SO_4; W-3: 5 mL HNO_3 + 0.5 mL H_2SO_4 + 1 mL $HClO_4$; W-4: 3 mL HNO_3 + 9 mL HCl)*

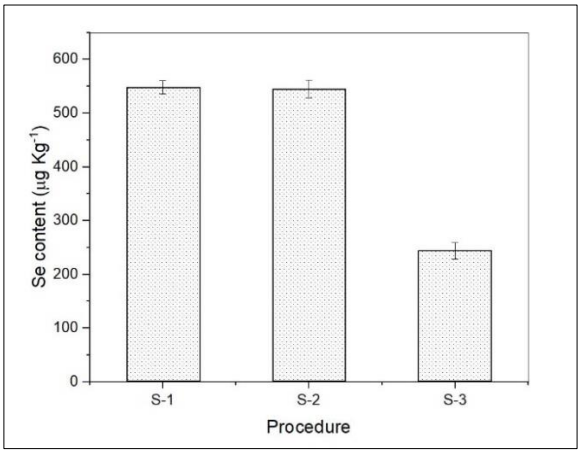


Figure 4. *Efficiency of sediment sample preparation using different acid mixtures (m_{sample}= 1g (n=5); S-1: 10 mL HNO_3 + 1 mL H_2SO_4 + 2 mL $HClO_4$; S-2: 10mL HNO_3 + 1mL H_2SO_4 + 4mL $HClO_4$; S-3: 3mL of HNO_3 + 9mL of HCl)*

3.3. Performance of analytical methods for selenium analysis in sediment

The efficiency of sample preparation for Se measurement in sediment is shown in Figure 4. The results show that the S-3 procedure using the HCl: HNO_3 mixture did not completely digest the sediment matrix. Although this mixture presents strong oxidizing properties, the evaporation temperature is low. It is ineffective for the sediment sample when determining metal(loid)s such as selenium. This phenomenon can be attributed to untreated organic substances reducing Se^{VI} to Se^{IV} forms, whose volatile compounds are easily lost during sample decomposition. S-1 and S-2 procedures are characterized by higher temperatures by using H_2SO_4, and in combination with the strong oxidizing agent as $HClO_4$, these acid mixtures are more efficient and stable than the S-1 procedure. In contrast, using 4 mL $HClO_4$ in the S-2 procedure did not obtain better results than in S-1 using only 2 mL $HClO_4$. The S-2 procedure was re-evaluated for efficiency by recovering the standard addition on a high TOC matrix (180 mg g^{-1}). With high TOC, the sample preparation still achieved good efficiency, i.e., selenium recoveries ranged between 95% - 97% for all

investigated Se concentrations, including 2, 10, and 20 µg L^{-1} (Figure 5). For reproducible assessment, the present study measured Se contents in sediment samples over different days, i.e., 4 days within 2 weeks (n = 3/ each day) (Table 2). According to the Horowitz formula, the favorable value of $S_{r_{max,r\%}}$ at a concentration of 561.2 µg L^{-1}, i.e., $S_{r_{max,r\%}}$ =12 > 5.5%. Thus, the result demonstrated good reproducibility.

The method limits of detection and quantification were estimated by analyzing 11 blank samples prepared by the S-1 procedure. The solutions were diluted 50 times before selenium measurement on HG-AAS. The absorbances of 11 blank samples were as follows 0.01457, 0.01453, 0.01423, 0.01424, 0.01482, 0.01570, 0.01643, 0.01640, 0.01641, 0.01620, 0.01613. MDL and MQL were 13.6 µg kg^{-1} and 45.2 µg kg^{-1}, respectively. According to Appendix F of AOAC (2016) [19], the results demonstrated a favorable method of recovery and repeatability. Furthermore, the S-1 procedure was used for digestion to quantify Se content in Mess-3 (n = 3). The measured selenium content was not significantly different compared to the certified value, i.e., 0.72 ± 0.03 mg kg^{-1} *vs* 0.72 ± 0.05 mg kg^{-1} (t_{TN} = 0.478 < $t_{0.95,5}$=2.571), respectively. As a result, the proposed method has high accuracy and can be widely applied to determine selenium in sediment for environmental monitoring and management.

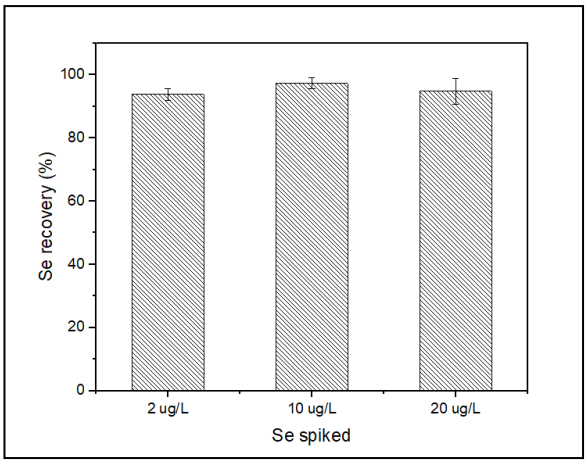


Figure 5. *Selenium recovery in high TOC sediment matrix (up to 180 mg g^{-1})*
(Spiked Se standard:2, 10, 20 µg L^{-1}; S-2: 10 mL HNO_3 + 1 mL H_2SO_4 + 2 mL $HClO_4$, n=5)

Table 2. *The measured values of selenium content in sediment samples over different days*

Time	Se content (µg kg^{-1})	RSD (%)
Day 1	580.4	2.8
Day 2	548.3	2.3
Day 3	544.6	3.0
Day 4	571.3	2.8
Average	**561.2**	**2.8**

4. Conclusion

The proposed analytical method for determining selenium content in wastewater and sediment has been successfully evaluated in a laboratory. Various analytical parameters related to the sample preparation procedure hydride generation were investigated to discover the optimized working parameters. The 3M HCl was favorable for sample dilution and reaction conditions of hydride forming on HG-AAS. The sample preparation achieved good performance for wastewater samples using a mixture of HNO_3 and H_2SO_4. The MDL was 0.088 µg L^{-1}. For sediment samples, the mixture of HNO_3: H_2SO_4: $HClO_4$ demonstrated a high efficiency to completely digest the matrix composition. The MDL reached 13.6 µg kg^{-1}. The study highlighted

that the analytical method can be applied further to various sediment samples, river water, and wastewater for research and management purposes.

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