

Adaptation of the methodology for sequential five-step fractionation of elements from bottom sediments of lake Imandra

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Abstract. A series of experiments was carried out to adapt the technique of five-stage sequential fractionation of elements from soils, silts and bottom sediments (on the example of bottom sediments of Lake Imandra). The factors influencing the research by the method of five-stage sequential fractionation of elements from bottom sediments are considered. The results of changing the parameters of the extraction process are presented. The requirements for successful realization of experiments are formed. Application of adapted methodology for assessment of potential negative impact of pollutants in the system “bottom sediments - water” by fractionation of elements by physical and chemical mobility, potential bioavailability of elements in bottom sediments is proposed.

1 Introduction

Lake Imandra, located in the western part of the Kola Peninsula, is the most exposed to anthropogenic impact. Limited species composition and short food chains, in cold latitudes, accelerate degradation processes under abiotic impact on water bodies in the Far North. The catchment area of the largest lake in the Murmansk region hosts several industrial enterprises. These include mining companies such as OJSC Apatit, Apatity, and Kirovsk. It also includes metallurgical enterprises like Kola MMC, OJSC Severonickel, and Monchegorsk. OJSC Olkon in Olenegorsk represents iron ore production. The area also contains energy facilities, including Kola NPP, Apatitskaya TPP, and the Nivsky HPP cascade. About 170 thousand people live in this region. Federal highways and railways run along the shores of the reservoir.

The form of their presence in environmental objects (soil and water bodies) determines ecological hazard and toxic properties of pollutants. The ecological hazard directly relates to the ability of pollutants to form complexes and their potential bioavailability in specific conditions of natural water bodies. Bottom sediments are an informative source for assessment of water body pollution taking into account their adsorption properties. Data on the chemical composition and forms of pollutants in bottom sediments are used to determine the bioavailability of various elements in the ecological system. They are also used to establish the transport processes of pollutants in aquatic systems and in the

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environment in general. In addition, such data are important for the evaluation of geochemical cycles.

Sequential extraction (fractionation) techniques are used to determine the forms of contaminants (e.g. heavy metals) in sediments, soils and muds. These techniques allow the determination of the forms of occurrence and behaviour of different pollutants, such as heavy metals, in different fractions of bottom sediments. There are a large number of fractionation schemes authored by: McLaren, Crawford, Tessier, Campbell, Bisson, Kersten, Ferstner, Tsaen, Brummer, Krishnamurthy, Huang, Van Rees, Kozak, Rostad and others, however, none of them is universal and preferable.

The five-step sequential extraction technique is widely used for soil research. It is described in sources. This technique consists in extraction of elements from bottom sediments. Successive leaching reagents carry out extraction. (Table 1). The sequence of solutions used is determined by the degree of leaching. The advantage of this technique is greater selectivity in the extraction of fractions, as well as minimisation of "fraction overlap".

Table 1. Five-step scheme for the sequential extraction of metals.

EEstep	Leached fraction	Biological availability	Metal species
11	Exchangeable–watersoluble (0.05 M Ca(NO ₃) ₂)	Easily accessible	Ions bound to the sample matrix by weak electrostatic interactions
22	Acid-soluble (0.43 M CH ₃ COOH)	Easily accessible	Specifically adsorbed ions
33	Readily reducible (0.1 M NH ₂ OH HCl (pH 3.6))	Moderately affordable	Elements bound to amorphous manganese oxides
44	Readily oxidizable (0.1 M K ₄ P ₂ O ₇ (pH 11))	Moderately affordable	Elements bound to humates and fulvates
55	Hard to repair (0.1 M (NH ₄) C ₂ O ₄ (pH 3))	Hardly reducible	Elements bound to amorphous iron oxides

2 Purpose of work

This article discusses the key problems encountered when studying sediments using the five-step sequential extraction technique on soils, silts, and sediments. It also analyzes the causes of these problems and proposes potential solutions. Bottom sediments are complex mixtures of minerals, organic matter, anthropogenic inclusions, and living organisms. This heterogeneity adds complexity to the extraction process and can significantly influence research outcomes. Studying Lake Imandra's bottom sediments is crucial to obtain pertinent data regarding heavy metal mobility within the "sediment-water" system and assess anthropogenic impact. This information is particularly vital considering the natural variability of the studied environment. Element fractionation methods based on physicochemical mobility offer an effective tool for acquiring more precise information on the potential bioavailability of pollutants in bottom sediments. Refining the five-step sequential extraction methodology for bottom sediments is critical to obtain more accurate data on mobile contaminant forms, including heavy metals. These data are essential for making well-informed environmental decisions.

3 Materials and methods

Bottom sediments of Lake Imandra.

Date of sampling: 18.03.2020.

Location: Vysokiy Island.

Depth of sediment column sampling: 8 metres.

Speaker height: 25 cm.

The sediment column was divided into 1 cm layers. There were 25 such layers in total. The samples were stored at -5°C . In the studies described below, three layers of this column were studied. These are the surface layer (1-2 cm), the middle layer (12-13 cm) and the bottom layer (24-25 cm). The samples contain about 25 per cent water. After thawing, the bottom sediments were placed in a centrifuge to separate them from the pore water. Centrifugation was carried out for 3 minutes at 1000 rpm.

3.1 Reagents

Reactants used to prepare leaching solutions $\text{Ca}(\text{NO}_3)_2$ (analytical grade), CH_3COOH (analytical grade), $\text{NH}_2\text{OH}\cdot\text{HCl}$ (chemically pure), $\text{K}_4\text{P}_2\text{O}_7$ (chemically pure), $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (chemically pure), HNO_3 (high-purity grade), KOH (chemically pure) was used for pH adjustment.

A five-step sequential extraction procedure was performed on the samples using a specialized apparatus, depicted in Figure 1. This apparatus consists of a microcolumn, with a schematic representation provided in Figure 2. The extractant is delivered to the microcolumn containing the sediment sample via flow paths using a peristaltic pump at a flow rate of 1 mL/min. The flow paths are comprised of 1 mm diameter plastic tubing connected to flexible tubing at both ends. The peristaltic pump's rotating rollers compress the flexible tubing and its contents. The rotation of the rollers propels the leaching solution through the tubing, directing it through the flow paths and into the microcolumn.

The extracted fractions (eluates) are collected in a cylinder. A volume of 60 mL of extractant is required for the complete leaching of elements from each fraction. Consequently, the leaching of a single fraction necessitates 1 hour. It is crucial to maintain a continuous and precisely ordered supply of extractants with specific leaching properties. This meticulous control applies to both the sequence and volume of solution delivery.

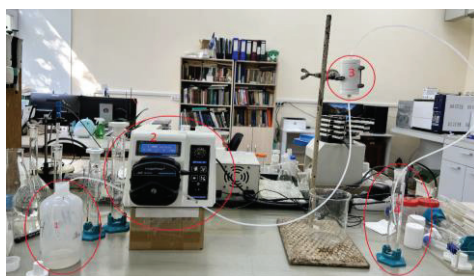


Fig. 1. Experimental Extraction Setup.

1 - Leaching Solution Reservoirs:

- 0.05 M $\text{Ca}(\text{NO}_3)_2$.
- 0.43 M CH_3COOH .
- 0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$.
- 0.1 M $\text{K}_4\text{P}_2\text{O}_7$, pH 11.
- 0.1 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$, pH 3.

- 2- Peristaltic Pump (BT100-1F).
- 3- Microcolumn No. 2 (Figure 2).
- 4 - 100 ml Graduated Cylinder for Eluate Collection.

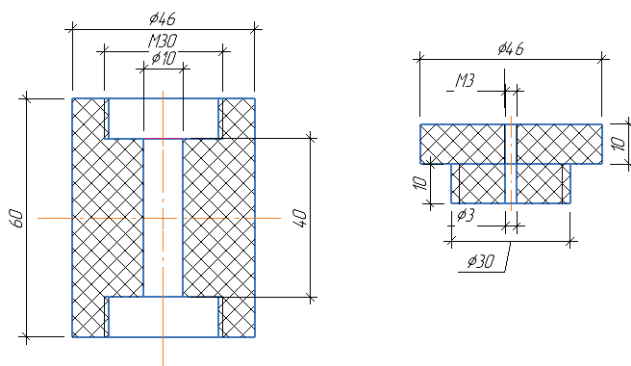


Fig. 2. Schematic Diagram of Microcolumn No. 2.

3.2 Methods

1. The moisture content of the sample was determined by drying a 5 g sample. The sample was placed in a desiccator at 105 °C for 6 hours. The moisture content of the samples was:

- 1-2 cm - 78.8 %.
- 12-13cm - 81%.
- 24-25cm - 85%.

2. Prior to commencing the extraction procedure, the fluid volume within the flow paths was determined. This was achieved by passing a known volume of distilled water through the system, initiating at the inlet of the flow path tubing, passing through the microcolumn, and collecting the effluent at the outlet. The volume of the collected water was then measured using a graduated cylinder. In this experimental setup, the fluid volume within the flow paths was determined to be 5 mL. This volume was subsequently accounted for during fraction collection by subtracting it from the total collected volume.

3. Before each experiment, the column was washed for 30 minutes with a mixture consisting of 300 mL of distilled water, 50 mL of ethanol, and 2 mL of concentrated nitric acid (HNO₃). The flow rate was 1 ml/min. The sample suspension was then placed in a microcolumn. When the sample was placed, a cellulose acetate membrane and silicone spacers were placed over the holes in the top and bottom of the column, and then the top and bottom caps were screwed on.

Each experiment involved the sequential collection of five fractions, obtained by passing the five leaching solutions consecutively through the microcolumn. The change between leaching solutions was performed without interrupting the flow. Since the target eluate volume for each fraction was 60 ml, the leaching solution was switched when 55 ml of eluate had been collected. This ensured that the remaining 5 ml of solution in the tubing system, containing remnants of the previous leaching solution, were flushed out and replaced by the next solution. The extracted fractions were numbered sequentially as follows:

The extracted fractions were labelled with a through numbering to ensure unambiguous identification of each extraction step:

- Fraction: exchangeable using 0.05 M Ca(NO₃)₂.
- Fraction: acid-soluble - 0.43 M CH₃COOH.

- Fraction: Easily reducing - 0.1 M $\text{NH}_2\text{OH HCl}$ (pH 3.6).
 - Fraction: easily oxidised - 0.1 M $\text{K}_4\text{P}_2\text{O}_7$ (11 pH).
 - Fraction 5: difficult to recover - 0.1 M $(\text{NH}_4) \text{C}_2\text{O}_4$ (3 pH).
- Three parallel experiments were performed for each sample.

4 Results

A series of experiments revealed that the following parameters could be adjusted to optimize the five-step sequential extraction method for sediment samples:

- Microcolumn type.
- Flow direction.
- Sample mass.
- Membrane pore size.

The following section presents the results of these experiments, highlighting several challenges encountered. These challenges necessitate further analysis and refinement of the methodology.

4.1 Experiments Yielding Unsatisfactory Results

An unsuccessful experimental outcome is defined by the inability to collect all five fractions in the required volume of 60 mL.

4.1.1 Experiment 1

The initial series of experiments employed Microcolumn No. 1, possessing a design akin to that illustrated in Figure 2, with an internal volume of 0.5 mL. The leaching solution was directed downwards, and a 0.5 g sample (Sample 1-2) was utilized. The first 60-minute stage yielded a 60 mL fraction. However, during the subsequent 120-minute stage, the collected fraction volume decreased to 40 mL. This stage was marked by the appearance of droplets at a flow path connection, signifying a leaching solution loss of approximately 1 mL/min. In the third stage, spanning 150 minutes, the collected fraction volume further diminished to 30 mL, while the leakage rate at the flow path connection increased to 2 mL/min. The fourth stage, lasting 30 minutes, yielded only a 10 mL fraction. Critically, this stage witnessed a separation at the junction of the flexible and plastic flow path tubing, likely due to elevated pressure within the system. Consequently, the experiment was halted after the fourth stage due to significant leaching solution loss and compromised system stability.

4.1.2 Experiment 2

Microcolumn No. 1 was used. The flow direction of the leaching solution was set from top to bottom. The weight of sample 1-2 was 0.25 g. Three fractions of leaching solution were taken. The volume of each fraction was 60 ml. The sampling took 180 minutes. In the fourth step, a solution leak occurred. The leak occurred at the connection point between the flexible tubing and the plastic tracks. The rate of leakage was 1 ml/min. This slowed down the extraction of the fourth fraction. The volume of eluate extracted was 40 ml in 150 minutes. This circumstance prevented the completion of the experiment. The fifth fraction could not be obtained.

Conclusion: Two fractions were extracted using a 0.5 mL microcolumn #1 with a 0.5 g suspension. The extraction time of the second fraction increased significantly. The loss of

leaching solution exceeded the flow of solutions into the microcolumn. A positive dynamics was observed when reducing the suspension by two times. It was noted at the stage of selection of the first three fractions. The extraction of the fourth fraction was interrupted due to increased pressure in the system.

4.1.3 Experiment 3

A subsequent experiment utilized Microcolumn No. 2, characterized by a larger internal volume of 1 mL, while maintaining a downward flow direction. A 0.5 g sample (Sample 12-13) was employed. The initial three fractions were collected without significant deviations. However, during the fourth stage, a solution leakage emerged due to a loss of system integrity. Despite this leakage, approximately 40 mL of the fourth fraction eluate was collected over 150 minutes. The leaching solution was then replaced for the fifth fraction, yielding 30 mL of eluate over 180 minutes. The experiment was subsequently terminated due to ongoing leaching solution losses and a decline in the extraction rate.

4.1.4 Experiment 4

In order to eliminate the leakage problem in the third experiment, microcolumn No. 2 was used. The flow direction was changed to "bottom-up". The tightness of the system was increased by optimising the connections. This was done by rolling the ends of plastic tubes. The mass of the sample remained the same - 0.5 g. After collecting the first three fractions, the microcolumn was placed in a refrigerator for 24 hours. This was done to stabilise the conditions. Placing the microcolumn with the sediment sample in the refrigerator is necessary for the correctness of the experiment. This procedure should be done in two repetitions. Next, the results should be compared with those obtained without freezing the sample. If there are no significant differences, we can talk about the correctness of this procedure. At the stage of collecting the fourth fraction, there was an obstruction in the conductive pathways. This caused an increase in pressure in the system. Droplets formed at the junction of the flexible tubing and plastic pathways. Leaks were 1 ml/min at the junction. This was accompanied by disconnection of the conductive pathways. The experiment was terminated. The reason was the loss of leaching solution during disconnection of the connections.

Conclusion: Using a 1 ml microcolumn with a top-down flow direction did not give any improvement. In the fourth experiment, changing the flow direction and dividing the experiment into two parts did not eliminate the problem.

4.1.5 Experiment 5

In this experiment, microcolumn No. 2 was used. The flow direction of the leaching solution was set from bottom to top. The weight of the sample 24-25 was 0.25 g. The first three fractions were selected successfully. The volume of each fraction was 60 ml. The duration of each fraction was 60 minutes.

In the fourth step, which lasted 60 minutes, a fourth fraction of 10 ml was collected. The conductive pathways lost integrity due to the increased pressure in the system. Holding the disconnection point of the flexible tubing and plastic tubing did not yield positive results. It did not prevent the loss of leaching solution. After disconnecting the tubing, no leach solution entered the microcolumn. Disconnection was instantaneous due to the high pressure in the system.

At the fifth stage the experiment was terminated due to significant losses of leaching solution. The system was unstable.

4.1.6 Experiment 6

To eliminate the problem with pressure rise in the system, sample 24-25 was used in the sixth experiment. It was pre-dried for 16 hours at +5 °C. A 0.25 g sample weight was placed in a Teflon tube with an open lid. The test tube with the sample was stored in the refrigerator. The sample was stored for 24 hours at +5 °C. Thus, the sample was dried without complete loss of moisture. Three fractions were sampled within 60 minutes. The volume of each fraction was 60 ml. In the fourth step, which lasted 60 minutes, a fourth fraction with a volume of 10 mL was collected. The conductive pathways lost integrity due to the increased pressure in the system. Holding the disconnection site of the flexible tubing and plastic tubing did not yield positive results. After disconnecting the tubing, no leach solution entered the microcolumn. The disconnection was instantaneous due to the high pressure in the system. In the fifth step, the experiment was terminated. The reason was significant losses of leaching solution and unstable operation of the system.

Conclusion: The results of the experiment with halved sample mass showed that drying the sample for 16 hours did not solve the problem. Problems with increased pressure in the system and disconnection of conductive pathways remained.

4.2 Experiments with successful results

A successful experimental outcome is defined by the successful collection of all five fractions, each with the required volume of 60 mL.

4.2.1 Experiment 1

The first experiment was carried out with microcolumn No. 2. The sample 12-13 with a 0.5 g sample weight was placed in it. The flow of solvent was directed from bottom to top. This provided a more uniform passage of the solvent through the sample. The peculiarity of this experiment was the preliminary preparation of the sample. The column with the sample suspension was placed in a refrigerator after the extraction of the three fractions. The storage lasted for three weeks. Thus, the experiment was divided into two parts. After three weeks storage in the refrigerator, the column was removed. The extraction process was continued. The parameters for the remaining two fractions remained similar.

The result of the experiment was considered successful. All five fractions were successfully extracted. Presumably, storing the micro-column with the sample helped to reduce the moisture content of the sample. This may have improved the extraction process. However, splitting the experiment into two parts is undesirable. It may distort the results due to prolonged storage of the sediment sample.

4.2.2 Experiment 2

The second experiment was carried out with the same microcolumn No.2. Sample 1-2 was used. The mass of the sample was halved and was 0.25 g. The direction of flow was kept, it was from bottom to top. In this experiment, special attention was paid to the tightness of the system. The airtightness was reinforced. This was done to prevent leaks that could lead to loss of extractant. Loss of extractant could have increased the extraction time of the fractions.

Five fractions were also collected in this experiment. The first three fractions totalled 60 ml each in 60 minutes. This was as in the previous experiment. However, when the fourth fraction was collected, a brief loss of tightness was recorded. The conductive pathways lost tightness once. Once it was restored, the connection of the conductive pathways at the

junction was resumed. Collection of the fraction was continued. Eventually, the fourth fraction was recovered in the required amount. However, the extraction took 65 minutes instead of 60 minutes. The last, fifth fraction was extracted in the standard 60 minutes.

Conclusion: Although cooling the sample in Experiment 1 may have had a positive effect, it is the improved tightness in Experiment 2 that is the more likely factor that provided the positive result.

4.2.3 Experiment 3

The third experiment was carried out with sample 1-2. The mass of the sample was 0.25 g. The direction of the extractant flow was bottom-up, as in the previous experiments. In this experiment, despite halving the mass of the sample compared to the previous experiments, there was a problem with the tightness of the system.

The first three fractions were obtained without difficulty. Each fraction totalled 60 ml in 60 minutes. However, during collection of the fourth fraction, loss of tightness of the conductive pathways was observed. After collecting 30 ml of eluate, there was a separation at the junction of the flexible tube and the conductive pathways. This was caused by an increase in pressure.

To prevent the experiment from being interrupted, the junction of the conductive pathways was held forcefully. This continued for 30 minutes. Next, the membrane was ruptured due to the increase in pressure. Despite this incident, the experiment was successfully completed. The fifth fraction was extracted in the standard 60 minutes.

4.2.4 Experiment 4

The fourth experiment was conducted with sample 24-25. The mass of the sample was 0.25 g. The sample was dried for 66 hours before starting the experiment. The first three fractions were collected without difficulty. The volume of each fraction was 60 ml in 60 minutes.

During the collection of the fourth fraction, an increase in system pressure was recorded. This resulted in disconnection of the conductive pathways after collecting only 10 ml of eluate. Despite attempts to hold the disconnection site, membrane rupture occurred. The experiment was continued. The sample was allowed to enter the eluate through the damaged membrane.

The fifth fraction was obtained in the standard 60 minutes. Despite the leakage problems encountered, both experiments were considered successful. All five fractions were obtained. Drying the sample in open air for 66 hours reduced the moisture content from 85% to 75%. The changes made in each of the experiments did not lead to an unambiguously positive result.

Conclusion: Both experiments encountered the problem of disconnection of the conductive pathways. However, the problem was eliminated. Positive dynamics of the experiment was noted when the sample was dried for 66 hours. The following experiments were performed under the above conditions. Keeping the conductive pathways from disconnecting provoked membrane rupture. This improved the permeability of the leaching solution through the bottom sediment microcolumn.

4.3 Membrane selection in the extraction stage of the 4th fraction

The conducted experiments revealed a recurring challenge during the collection of the fourth acid-soluble fraction, specifically regarding the passage of the leaching solution through the microcolumn containing the sediment sample. When the sample was loaded

into the microcolumn, acetate-cellulose membranes were placed over the openings at both the top and bottom. However, these membranes obstructed the flow of the leaching solution, leading to elevated pressure within the system. This pressure buildup subsequently caused either damage to the flow path integrity or rupture of the membrane itself.

Four types of cellulose acetate membranes were used to determine the membrane with the best permeability. They had different pore sizes: 5 μm , 0.45 μm , 0.25 μm and 0.1 μm . This was done during the experiment during the acid-soluble fraction collection step.

When using a classical membrane with a pore size of 0.45 μm , after 10 minutes of fractionation, the leaching solution was obstructed. This caused an increase in system pressure, which caused the flexible tube and conductive tubes to separate. When the disconnection point was held by force, the leach solution flow burst through the upper membrane. This compromised the integrity of the membrane (Figure 3).

Thus, the pressure in the system dropped and permeability was restored. However, the sample suspension entered the eluate through the ruptured membrane.



Fig. 3. 0.45 μm membrane (left, top; right, bottom).

The membrane with a pore size of 5 μm was not subject to rupture. This over the course of the experiment provoked an increase in pressure and an impassability of the leaching solution. The experiment was terminated (Figure 4).

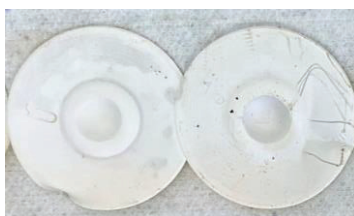


Fig. 4. 5 μm membrane (left, top; right, bottom).

The use of a thinner membrane with a pore size of 0.25 μm was accompanied by rupture of the lower part. This occurred after 5 minutes of eluate collection. The bottom sediment sample got into the conductive pathways and clogged them. The experiment was terminated (Figure 5).



Fig. 5. 0.25 μm membrane (left, top; right, bottom).

The application of a membrane with a pore size of 0.1 μm was accompanied by rupture of the lower part. This occurred 2 minutes after the start of the experiment. The rupture provoked the same scenario as in the application of the membrane with a pore size of 0.25 μm (Figure 6).

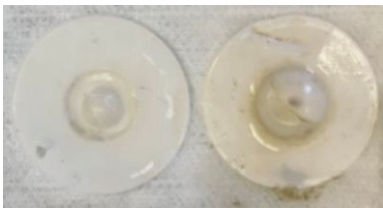


Fig. 6. 0.1 μm membrane (left, top; right, bottom)

5 Discussion

The duration of the extraction process of elements from one sediment sample takes on average 8 hours. This is possible provided that all 5 fractions are extracted successfully. In the subsection "Experiments with negative results", the extraction time of 3-4 fractions ranged from 6.5 to 7.5 hours. In this case, all required 5 fractions were not extracted.

The main difficulties in applying the technique of five-stage sequential extraction of elements from bottom sediments can be noted. These include pressure build-up in the conductive pathway system, membrane rupture, and leaching solution leaks from the microcolumn. These difficulties were most significant during the extraction phase of the fourth fraction. This provoked the decision to terminate the experiment.

Changing the type of microcolumn from a 0.5 mL internal volume to a 1 mL microcolumn and changing the flow direction reduced the number of experiments with negative results. However, this did not solve the problem associated with increased pressure in the system. Positive results were achieved due to the decision to reduce the mass of the sample suspension by a factor of 2 (from 0.5 g to 0.25 g dry weight). The use of bottom sediments with lower moisture content also contributed to this.

The algorithm of actions for the application of the five-stage sequential extraction of elements from sediments with adaptation is presented below (Figure 7).

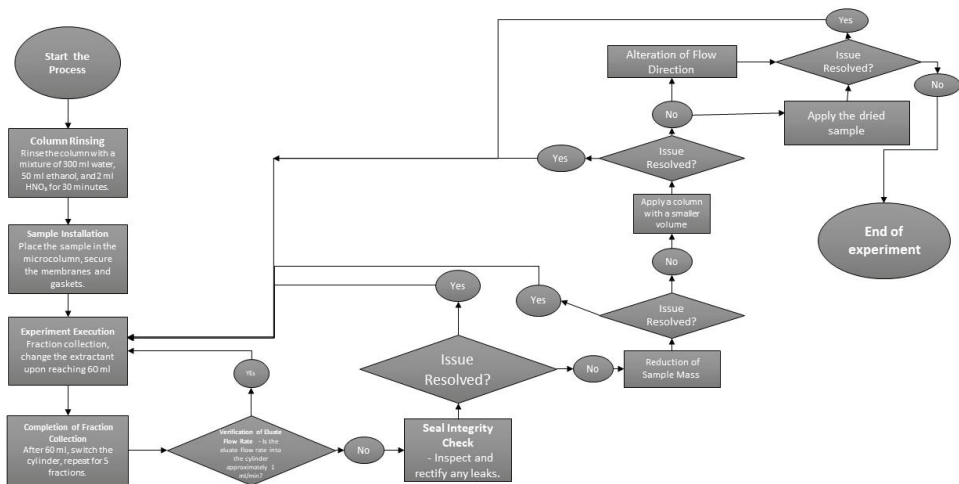


Fig. 7. Flowchart of the application of the five-step sequential feature extraction methodology with adaptation in mind.

6 Conclusion

A five-step sequential extraction procedure is employed in this study to accurately determine the potential bioavailability of elements from the sediment. Maintaining a continuous flow of extractant solutions is crucial for obtaining reliable results.

The following guidelines must be followed for a successful experiment. Firstly, it is critical to use a dried sample with a moisture content not exceeding 75%. Second, the flow direction of the incoming leaching solution into the microcolumn with the sediment sample should be bottom-up. Thirdly, the weight of the sediment sample should not exceed 0.5 g. Fourthly, a microcolumn with an internal volume not exceeding 1 ml should be used. Fifth, a cellulose acetate membrane with a pore size of 0.45 μm should be used.

During the adaptation of the five-step sequential extraction procedure for elements from bottom sediments, several challenges arose that require solutions for successful element extraction:

1. High System Pressure: Experiments revealed that pressure build-up occurs even when utilizing a bottom-up flow and reducing the sample mass to 0.25 g, leading to disconnections within the flow path. A comprehensive equipment modification is necessary, encompassing:

- Microcolumn Design Modification: Experimental results indicate the need to optimize the microcolumn design to ensure an optimal sample mass-to-volume ratio.
- Optimal Flow Parameter Selection: A more detailed investigation into the relationship between pressure, flow rate, and direction is required.
- Pressure Control System Enhancement: Implementing additional elements for pressure monitoring and release will help prevent flow path disconnections.

2. Sample Drying Efficiency: Drying the sample before leaching did not yield the expected increase in experimental stability. Further research is needed to explore the influence of bottom sediment moisture content on the extraction process and determine the optimal moisture level for analysis.

3. Optimal Membrane Selection: Membrane rupture was observed in several successful experiments, resulting in sample leakage into the eluate, potentially significantly impacting data accuracy. Membranes with pore sizes of 5 μm , 0.45 μm , 0.25 μm , and 0.1 μm were found susceptible to rupture at varying rates. Additional experiments are required to determine the optimal pore size that balances filtration speed and rupture risk.

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