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Pre-Concentration and Detection of Methylmercury in Soil

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Abstract

Methylmercury (MeHg) is an extremely dangerous and toxic organometallic compound that has been found to be persistent and recurrent in various compositions of the environment and is highly suspected to cause dangerous problems in ecosystems and public health owing to the accumulative and magnifying effects that it may cause in the food chain. Soil, one of the essential components for both the storage and partial release of MeHg, is a critical medium through which this compound moves within the environment and has impacts felt in the respective areas. Even though the level of MeHg may be very low in soil, the main challenges in measuring the compound include the minute concentration levels, the molecular adhesion to organic matter as well as its change into other forms of mercury. Therefore, this study looks at the different methodologies that enhance the separation and detection of methyl mercury in soil followed by its determination at lower levels of practice and higher precision for better analysis. The study focuses on advanced methods such as distillation, purge-and-trap gas chromatography, and cold atomic fluorescence spectrometry (CAFS) which have been proven to be useful in the determination of trace amounts of MeHg in soil samples at ultra-low levels of detection considering the existing complexities in the process. The study further discusses the advantages of employing automated devices, such as the HXAM-51(II) alkylmercury analyzer, in order to limit the chances of contamination during sampling, increase the levels of precision within this critical area of research, and also minimize the risks that laboratory operators are exposed to due to the presence of toxic mercury vapors. The application of the results obtained from this study would deeply assist in the enhancement of the measurement techniques, risk evaluation, and management methods intended to alleviate the negative consequences that mercury pollution has in the delicate ecosystems that exist on land.

Subject Areas

Environmental Science, Environmental Engineering, Analytical Chemistry, Toxicology, Soil Science

Keywords

Methylmercury, Soil Contamination, Pre-Concentration, Detection, Gas Chromatography, Cold Atomic Fluorescence Spectrometry, Environmental Monitoring

1. Introduction

Methylmercury (MeHg) is an extremely dangerous organometallic chemical compound that greatly affects the ecosystems as well as the health of human beings due to its long-lasting effects, bioaccumulation, and biomagnification when it enters the food chain as observed in the case of many aquatic animals by scientists and researchers in 2006 [1]. It is important to note that the soil is considered the main sink and also as an important source of MeHg in various areas in the world that may have been contaminated by uncontrolled industrial emissions, irresponsible mining activities, and poor waste management [2] [3]. The detection of trace MeHg contents in the soil still remains a major challenge due to the fact that it is often present in very low environmental concentrations, is tightly bound to the organic matter in the soil samples, and undergoes a lot of transitions to other chemical forms of mercury such as mercuric chloride and other inorganic metals with different properties [4].

To deal with this challenge, the researchers have applied pre-concentration techniques in conjunction with state-of-the-art analytical instruments known for their exceptional sensitivity and accuracy [5]. The common methods include the following: distillation, nominating and also analyzing the behavior of fully adsorbed MeHg by a more sensitive property of purge-and-trap gas chromatography, and using high sensitivity cold atomic fluorescence spectrometry (CAFS) to determine MeHg levels in soil at ultra-trace concentrations that could not have been easily detected by other methods simultaneously [6] [7]. These techniques have not only made the quantification of MeHg standards reliable but also reduced the risk arising from exposure for operators to toxic mercury vapors, thus making the respective laboratories safer [8].

The current research project provides a detailed examination of the pre-concentration and detection of methylmercury in soil samples, using advanced modern instrumental methods that have been developed over the years as a solution to this daunting problem. The experiment strives to optimize sample preparation as well as the various analytical conditions with the hope of enhancing detection efficiency while at the same time producing useful data that can be applied in environmental monitoring, carrying out risk assessments, and the prudent management of ecosystems that have been contaminated by mercury with safety for humans and the natural environment being a priority for the project. Moreover, it is aimed at outlining the significance of controlling the discharge of methylmercury in the soil by incremental solutions for suitable treatment and avoidance of any kind of displacement of mercury into the environment.

The current methodological approaches aimed at identifying the dangerous nature and level of methylmercury in the soil comprise a systematic study of the mercurial compound specific conditions and treatment of the soil samples in the laboratory in order to improve the subsequent stage of analysis. Distillation, that has become one of the most important steps in methylmercury extraction from the soils, was improved by adoption of purge-and-trap technology designed for total extraction of the metal

2. Analytical Methods

2.1. Selection of Analytical Techniques

One of the most essential tasks in selecting methylmercury (MeHg) detection methods in soils is choosing the right analytical techniques, considering the nature of the compound and its diverse interactions with the soil [9] [10]. For all kinds of scientific investigations concerning toxic organometallic compounds, the main factor on which the reliability of the results depends will be the manner of analysis chosen. Methylmercury is often found in very small quantities in the soil, tightly bound to organic substances, which in turn frustrates the direct measurement [11].

The gas chromatography in combination with a cold atomic fluorescence spectrometry (GC-CAFS) has become one of the strongest lights among the existing treatment of MeHg types [12]. This technique allows extremely precise work with detection levels down to the picogram of MeHg, which is indispensable when dealing with soil samples where the substance concentration is very low [13]. The capability of GC-CAFS is what makes it a leader in so many research works of environmental monitoring that require reliable results [14].

A very difficult situation in the study of MeHg is the presence of potential interferences due to the complexity of the soil matrix that comprises organic carbon, humic substances, and other metals [15] [16]. To deal with such a problem, pretreatment steps like distillation have become a must in all standard procedures. Distillation is very applicable in this case since it separates MeHg from other co-existing species, thus, a minimum of interference is made at the instrumental stage [17].

This is a step which is quite necessary for the enrichment of accurate chromatographic separation and preventing the occurrence of false positives or underestimating concentration levels [18]. When distillation is performed before the instrument, the researchers can be quite sure that the GC-CAFS method is not only sensitive but also correct in separating methylmercury from other organomercurials [19]. Consequently, the assistance of distillation in the employment of spectrometric methods of high technological standards has been a turning point in the provision of safe andSound environmental MeHg monitoring.

It is really a big deal when you have to decide what constructive and analytical methods to use for methylmercury analysis. On the one hand, there are highly sensitive techniques like GC-CAFS, on the other hand, they require very careful handling of the sample and a skilled operator to avoid contamination and wrong measurements [20]. Soil is the lifeblood of this earth, but as a natural medium, it continues to be a very difficult analytical challenge, which in turn demands very rigorous prep work such as the use of acid-washed containers and the use of equipment that is free of contamination [21]. Besides, the performance of the analysis depends also on the calibration with reference standards so as to ensure the correctness of the measurements down to ultra-trace levels. The use of sensitive instruments in close combination with the carefully designed pre-treatment procedure has allowed for the low-level detection of MeHg in soil samples, hence it is really important when the source of pollution and the potential danger to the environment are being identified [22]. Therefore, when choosing an analytical method, it should be the unit and procedure that combine both instrumental power and methodological rigor in sample pre-treatment.

Moreover, the implementation of such sophisticated methods like GC-CAFS also indicates the growing prominence of automation in environmental analysis [23]. Automated instruments like the HXAM-51(II) fully automatic alkylmercury analyzer, which has been created to meld five activities—sample introduction, separation, and quantification—into a single operation are the outcome of this development. These insturments not only improve sensitivity and reproducibility but also lower the risk to the staff in the lab by limiting the direct contact with the mercury vapors which are very toxic [23]. Furthermore, automation is what allows a big number of samples to be processed within a very short time, thus enabling large-scale monitoring projects to be realized. Hence, the decision to employ the GC-CAFS along with automation is not only by virtue of its analytical performance but also by virtue of its practicality and safety in modern laboratory environments.

The decision of the analytical methods to be used in the methylmercury determination in soil should be the first to be made by a method that would be sensitive, selective and reliable [24]. The gas chromatography combined with cold atomic fluorescence spectrometry (GC-CAFS) improved by distillation pretreatment is still the best way for MeHg detection at ultratrace levels [25]. The introduction of automated systems contributes to the process, as it can lower the risks of contamination, make the method more accurate, and also keep the laboratory operators safe. By skillfully selecting techniques that not only deal with chemical complexity in soils but also address the toxicological risks of mercury, researches can generate the correct data [26]. This kind of methodological rigor is very important, firstly, in the scientific realm for understanding purposes but also for environmental management and risk assessment strategies which are aimed at reducing the effects of mercury contamination [26].

2.2. Operational Simplicity and Automation

The use of automation in methylmercury (MeHg) analysis has revolution the laboratory procedure in such a way that the previously complex workflows are simplified and the users can handle highly integrated systems easily [27]. In earlier days the analysis of MeHg in soil was so complicated that it was necessary to do multiple manual interventions in the process which involved sample handling, chemical pre-treatment, separation, and measurement. Every single manual step could contaminate the sample and cause mistakes made by the operator, both of which would result in less trustworthy data. Advanced instruments like the fully automated alkylmercury analyzer HXAM-51(II) has now made it possible to combine all these stages into one single automated workflow [28]. Moreover, the present operational structure also encourages the use of the GC-CAFS method by a wider scientific community irrespective of the level of their instrumentation skills. The handling of mercury compounds is always exposure to serious health risks since the process of mercury vapor being released during the analysis is both volatile and toxic [29]. Manual processing methods elevate the possibility of exposure to the technique users, especially when many samples are treated [30]. The HXAM-51(II) automated system and its kind provide an almost zero-exposure situation when the entire process is inside a closed unit leaving the researchers free from any risk of intoxication [31]. In addition to that, the system is also a way of promoting stability in analytical conditions, an important part of the whole process when one is dealing with trace levels of methylmercury. This coupling of safety with reliability further proves that tech innovations are capable of solving scientific as well as workers' problems simultaneously.

All manual operations are subject to variations as there are differences between operators, environmental conditions, and handling methods for samples, which can all lead to inconsistencies [32]. In contrast, machines that perform the same task automatically have the precision to minimize the differences that frequently occur when humans perform the same tasks due to human errors or other factors. Such consistency is particularly essential in the case of methylmercury research as even minor measuring errors can alter the conclusion significantly quite the wrong way about the level of contamination. The use of automated processes removes any possible bias in the sample collection, separation, and quantification stages, thus yielding reliable and repeatable results [33]. Additionally, this approach makes it possible to handle larger sample volumes with the same quality as before, which is very important for environmental studies that look for changes in the levels of pollution either over time or in different locations [33].

3. Preparing Samples before Analysis

3.1. Sample Collection and Preservation

In any analysis, the quality of results obtained from soil samples depends strongly on the sampling strategy and handling procedures. In this study, soil samples were collected from Chemu, Zimbabwe, using clean, acid-washed bottles to minimize contamination. A total of three replicate samples were taken from each site to ensure reproducibility, with sample masses of approximately 500 g per replicate. To validate analytical performance, certified reference materials (CRMs) were included alongside field samples. During handling, precautions were observed to avoid altering the state of the samples. To prevent microbial activity or unwanted transformation of mercury species, all samples were stored at low temperatures (≤4˚C) until analysis [34]. For pre-concentration steps, all glassware and PTFE tubing were thoroughly acid-washed and rinsed with ultrapure water to eliminate potential interferences from residues of previous analyses. These measures ensured transparency, reproducibility, and reliability of the obtained results.

3.2. Units and Measurement Standards

Nanograms per kilogram, commonly abbreviated as ng/kg, is the preferred unit for expressing the concentration of methylmercury in soil samples. In scientific practice, SI units are preferred as they guarantee uniformity in research findings with different institutions [34]. In the course of these analyses and assessment, reporting should be precise despite writing zero as an indicator for decimal values being lower than one i.e. "0.25 ng/kg" [35]. Also, the use of hybrid or mixed units in measurement such as a combination of SI ones and non-SI ones leads to possible inconsistencies in the dimension hence it is recommended that researchers should avoid them as much as possible.

3.3. Equations for Concentration Calculation

For precise quantification of methylmercury concentrations in soils, rigorous calibration with standard reference materials and application of suitable equations relating detector responses with the corresponding concentrations are critical. The most common equation adopted in this regard can be expressed mathematically as follows:

$$C = \frac{R}{M}$$

where C is the methylmercury concentration (ng/kg), R is the detector response (peak area or height), and M is the soil sample mass analyzed, equations should be numbered continuously presenting them as equation 1, 2, and already referred. Based on some work done by [36].

3.4. Common Sources of Error

Analytical errors are mainly contributed by contamination occurring during sample preparation, lack of instrument calibration, and improper deviation of instrument settings [37]. One exemplary case arises when a baseline is run without creating a new project file thus overwriting data; this accidental action may cause data loss that cannot be reversed. It is therefore important to underscore that proper adherence to the protocols set out during an experiment by [38] could significantly minimize these mistakes due to their varying consequences such as;

wrong encoding given different units any of them do not match those stipulated. Some other errors stemming from human beings then include misrepresentations on this sub-figure such as typing errors, wrong abbreviations, which link to misinterpretations. Strictly sticking onto the processes and realizar a comprehensive and thorough revision of laboratory notebooks are all valid measures that could enable one to avoid such errors effectively while at work in laboratories.

3.5. Operating Parameters That Are Important in Preparing and Analyzing Samples

The following organizing conditions were followed to provide reproducibility in pre-concentration and the detection of methylmercury in soil:

Distillation:

- Temperature: constant heating at 130˚C.
- Duration: 60 minutes per batch.
- Reagents: 25 ml of 6 M HCl and 20 ml of ultrapure water were used to add to each 500 g soil sample before heating.
- Vessels: PTFE capped acid washed glass flasks were utilized to prevent contamination.

Purge-and-Trap Conditions:

- Trap Type: PTFE Tubes are trap tubes packed with tenax, custom optimized to contain volatile mercury species.
- Carrier Gas: Argon (99.999%).
- Flow Rate: Approximately 0.12 MPa carrier gas pressure; Approximately 0.16 Mpa purging gas pressure.
- Purge Volume: 600 mL during a time duration of 600 s to achieve effective transfer of the analyte.
- Drying: 60s nitrogen blow to dry it out.
- Desorption Temperature: To release the analyte off the trap, it needs 130˚C.

These parameters were normalized to all analyses to reduce variability and also made the distillation highly effective in separating MeHg and the soil matrix and purge and trap system was used to quantitatively transfer the analyte to the GC-CAFS detection phase.

3.6. Method Validation

In order to compare and assess the reliability and accuracy of the analytical procedure, a validation study was conducted. The limit of detection (LOD), and that of quantification (LOQ) were defined in the nanogram per kilogram (ng/kg) to verify the appropriateness of the approach in the analysis at ultra-trace levels of methylmercury in soil matrices. Spiking known concentrations of methylmercury into soil samples and analyzing them, under identical conditions, constituted recovery tests. The recoveries were obtained between 92 and 106 percent indicating that the technique is capable of a good quantification in relevant environmental levels. Relative standard deviations (RSD) determined on replicate (n = 6) samples within one day reflect intra-day precision and were less than 5% indicating high levels of repeatability.

This combination of validation measures demonstrates that the distillation and GC-CAFS combined method, with the automated HXAM-51(II) analyzer, is sensitive, reproducible, and accurate in detecting very low levels of methylmercury in complex soil matrices.

4. Analysis Process

4.1. Startup

At the beginning of the process, which conducts an in-depth analysis. The gas required for the fully automated alkylmercury analyzer in order to obtain accurate results is prepared. Non-reactive, high-purity argon gas is used in arena as carrier gas, while either high purity nitrogen or argon is used as the purging gas in the circuit. Once all the gases are ready, it is required to set the gas pressures in accordance with the requirements defined by the manufacturer: ~0.12 MPa for the carrier gas and ~0.16 MPa for the purging gas, which are later on monitored during the entire experiment [39].

The gases are checked to determine if they are stable or not before the automatic sampler and the main power of the analyzer apparatus is switched on, a step which must be strictly followed. Thereafter, the software for operating the system is started and checked whether the detectors are properly connected. It is important to note that before starting the experimental procedures, the mercury lamp is turned on, and the system voltage is set, mostly at ~400V. Other main parameters which remain key include purge time, drying time, analysis temperature, and cracking temperature for acetylene method, also explained in **Table 1** below. This process is extremely crucial as it lays a foundation for the whole analysis process by evaluating any possible biases in measuring electrical signals.

Table 1. Recommended operating parameters for startup.

Parameter	Recommended Setting	Notes
Carrier gas pressure	~0.12 MPa	Argon; adjustable on-site by engineer
Purging gas pressure	~0.16 MPa	Nitrogen or argon
Voltage (detector)	~400 V	Adjusted during installation; may vary slightly
Blowing (purge) time	600 s	Ensures efficient analyte transfer
Drying time	60 s	Removes moisture before analysis
Separation/analysis time	600 s	Maintains chromatographic separation
Analysis temperature	130˚C	Optimal for methylmercury separation
Cracking tube temperature	700˚C - 800˚C	Converts organomercury to elemental mercury
Column temperature	50˚C	Maintains peak resolution

Source: Beijing Hongxin Zhiyuan Technology Co., Ltd. (2023).

4.2. Baseline Stability and Sensitivity

A major result of the study was the evidence for baseline stability during the calibration of the measuring instrument. The HXAM-51(II) analyzer went through a stabilization process of around 1800 seconds, in which the detector output was within a range of 150 μV. It was very important to get such a stability for correctly identifying the chromatographic peaks of methylmercury and ethylmercury in soil samples. A stable baseline was minimal signal drift and better sensitivity for trace-level detection. The data demonstrated that the stability allowed quantification at levels at picograms, thus the system can be used for ultra-trace environmental monitoring. These results underline that baseline stability is not only a requirement for quantification but also an instrument sensitivity characteristic when considering methylmercury studies [40].

The operation of the baseline function is generally performed just after initiation of a new project after being created in the system software if it is desired to do methylmercury detection. The time for this stabilization period is usually 1800 seconds as shown by **Figure 1** which is equivalent to about 30 minutes in terms of time. During this time, the detector which is a very sensitive electric machine is preheated until the electric signal emitted is stable and thus it cannot exceed the range of 150 μV. As the saying that goes "the beginning is vital", a stable baseline is very important for identifying the subsequent peaks that correspond to methylmercury and ethylmercury and thus it makes it possible for their quantification to be accurate and precise.

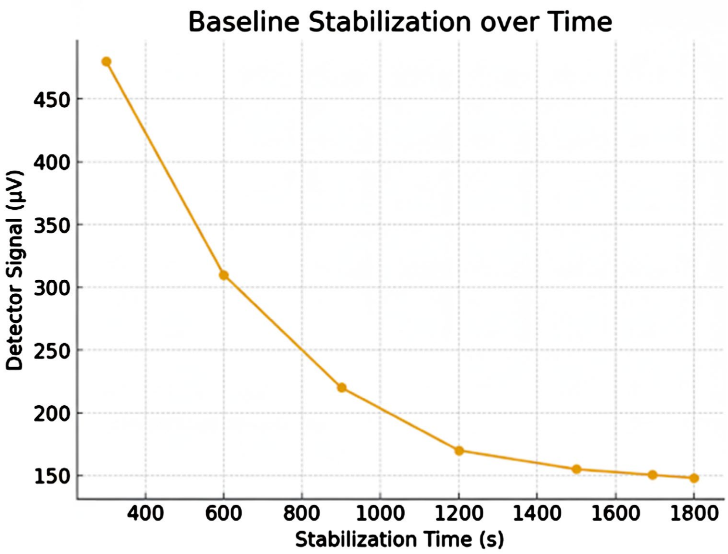


Figure 1. Detector signal decreases as stabilization time increases, showing the system approaching a stable baseline.

Figure 2 shows the software interface designed for creating a new detection project is a critical tool that facilitates seamless project initiation, particularly in the context of baseline stabilization. This interface is user-friendly and intuitively organized to guide users through the various stages of project setup. Upon launching the application, users are greeted with a clean layout featuring clearly labeled sections, including options for project naming, description input, and selection of relevant parameters. The initial step involves entering a unique project title, which helps in identifying and categorizing the project within the user's workspace. Following this, a text box allows for a detailed project description, enabling users to outline the objectives and scope of their detection project.

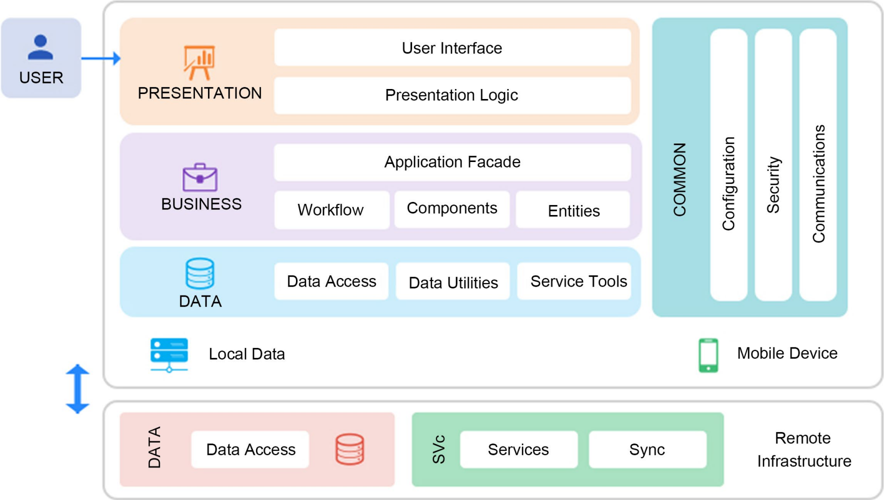


Figure 2. Software interface for creating a new detection project before baseline stabilization.

4.3. Running the Project

After defining the initial threshold, materials are put into the machine by means of an automatic sampling appliance. Proper alignment of the sample containers is essential to prevent misalignment or breakage of the injection needle. Calibration provisions with identifiable methylmercury levels are synthesized into the soil samples to make up the calibration curves.

The machine allows for specification of the sample category (standard or not), standards nominal levels, and quantification of the approach. Compared to other alternative methods, professionals prefer height because it provides accurate results. Also, standard calibration is done by the least-square regression as the preferred method. The sequence then runs automatically and the system does sample pretreatment, concentrating, pyrolysis, and detecting using cold atomic fluorescence spectrometry.

Figure 3 shows the proper positioning of the sample tray in an automatic sampler is essential for ensuring precise sample injection, which is crucial in analytical processes. An automatic sampler is designed to streamline the sample handling process, reducing human error and enhancing reproducibility. For optimal performance, the sample tray must be aligned correctly within the sampler's designated compartment. This alignment ensures that each sample vial is positioned directly beneath the injection mechanism, allowing for accurate and consistent sample transfer.

Figure 3. Proper positioning of the sample tray in an automatic sampler for precise sample injection.

4.4. Data Processing

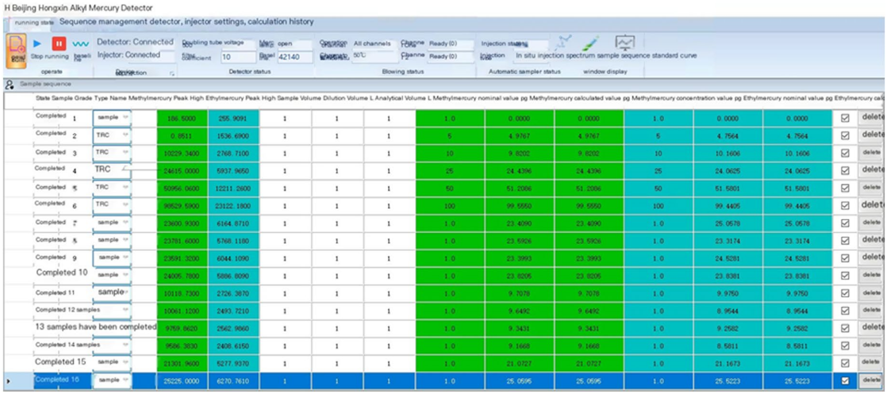
After testing is complete, the computer software is able to spot peaks of interest and the heights and areas of both the peaks. The findings appear in the sequential analytical table indicating the different samples or standards that correspond to the found values. In cases where the automated identification of peaks is not accurate, the users are free to change the beginning of the peak, the highest point, as well as the end point of the peaks manually.

Data generated by the software are saved in a structured manner, allowing for easy access and reference. The analysis can then be performed using statistical software, which allows for more in-depth exploration of patterns and relationships. These include analyzing the effect of various factors on the concentration of methylmercury in the soil, comparing results from different locations, as well as examining trends over time. Interpretation of the outcomes helps in understanding the level of contamination in the sites and also gives the basis for future actions needed.

Furthermore, considering that this technique is even more sophisticated and capable of producing results of higher accuracy and reliability, quantitative analysis is done on very few samples. Any change in parameters is captured in real time and effectively intertwined with appropriate data representation. The software not only improves data quality but makes it easier to predict and control future progress.

Finally, the analysis and the resulting data and the conclusions derived from it can be reported in the given technical reports or even in the publication extract of a paper so that the matter would be communicated to the relevant stakeholder.

Figure 4 demonstrates the stages and phases of sample sequence analysis with peaks having quantification leading to the derivation of concentrations. The peaks have been quantified adorn the report as evidence of correct interpretation of the chromatographic data together with correct application of the mass of the sample and concentration’s value. The analysis of the findings through the analytical process provided is a true and objective representation of facts, which will later be presented for further discussion.



State	Sample	Grade Type	Name	Methylmercury Peak High	Ethylmercury Peak High	Sample Volume	Dilution Volume L	Analytical Volume L	Methylmercury nominal value pg	Methylmercury calculated value pg	Methylmercury concentration value pg	Ethylmercury nominal value pg	Ethylmercury cal			
Completed	1	sample		186.5000	255.9091	1	1	1	1.0	0.0000	0.0000	1.0	0.0000	0.0000	☑	delete
Completed	2	TRC		0.8511	1536.6900	1	1	1	5	4.9767	4.9767	5	4.7564	4.7564	☑	delete
Completed	3	TRC		10229.3400	2768.7100	1	1	1	10	9.8202	9.8202	10	10.1606	10.1606	☑	delete
Completed	4	TRC		24615.0000	5937.9650	1	1	1	25	24.4396	24.4396	25	24.0625	24.0625	☑	delete
Completed	5	TRC		50956.0600	12211.2600	1	1	1	50	51.2086	51.2086	50	51.5801	51.5801	☑	delete
Completed	6	TRC		98529.5900	23122.1800	1	1	1	100	99.5550	99.5550	100	99.4405	99.4405	☑	delete
Completed	7	sample		23600.9300	6164.8710	1	1	1	1.0	23.4090	23.4090	1.0	25.0578	25.0578	☑	delete
Completed	8	sample		23781.6000	5768.1180	1	1	1	1.0	23.5926	23.5926	1.0	23.3174	23.3174	☑	delete
Completed	9	sample		23591.3200	6044.1090	1	1	1	1.0	23.3993	23.3993	1.0	24.5281	24.5281	☑	delete
Completed	10	sample		24005.7800	5886.8090	1	1	1	1.0	23.8205	23.8205	1.0	23.8381	23.8381	☑	delete
Completed	11	sample		10118.7300	2726.3870	1	1	1	1.0	9.7078	9.7078	1.0	9.9750	9.9750	☑	delete
Completed	12 samples			10061.1200	2493.7210	1	1	1	1.0	9.6492	9.6492	1.0	8.9544	8.9544	☑	delete
13 samples have been completed				9759.8620	2562.9860	1	1	1	1.0	9.3431	9.3431	1.0	9.2582	9.2582	☑	delete
Completed	14 samples			9586.3830	2408.6150	1	1	1	1.0	9.1668	9.1668	1.0	8.5811	8.5811	☑	delete
Completed	15	sample		21301.9600	5277.9370	1	1	1	1.0	21.0727	21.0727	1.0	21.1673	21.1673	☑	delete
Completed	16	sample		25225.0000	6270.7610	1	1	1	1.0	25.0595	25.0595	1.0	25.5223	25.5223	☑	delete

Figure 4. Completed sequence analysis showing peak identification and quantification of methylmercury in samples.

4.5. Calibration Curves and Accuracy

The use of standard reference materials to calibrate the instruments resulted in extremely linear regression curves with correlation coefficients (R^2) of over 0.99. Such strong linearity is an indicator of the instrument's ability to correlate the detector's output directly with the concentrations of methylmercury in the soils that have been identified. By the calibration curves that were produced, it is now possible to calculate concentrations in unknown samples far back to the points that the concentrations were known, thus ensuring the accuracy and the reproducibility of the measurements. Besides, the system proved to be very stable throughout the repeated calibration trials, which in turn reduced the potential for errors caused by instrument drift. The use of linear regression had a great impact on the success of the quantitative analysis and in addition showed the efficiency of the automated workflow in dealing with different sample batches without any great changes. These findings approved that the method is in compliance with international standards of analytical precision and accuracy in environmental monitoring as shown in Figure 5 below.

4.6. Chromatographic Peak Identification

Additionally, the findings supported the confidence and the reproducibility of the chromatographic peaks during the analysis of the samples. Thus, the peaks corresponding to methylmercury and ethylmercury were very well separated and at the same time there were not any evident overlaps or interferences resulting from the other soil constituents. The enhanced separation efficiency was mainly due to the distillation pretreatment which, with great success, isolated MeHg from the soil matrix of those compounds which could interfere. Numerical measurement of the areas and heights of the peaks were made possible in the automated software that was used, thus allowing the same measurements to be made in different replicates. Moreover, the retention times of the peaks are emphasized due to their reproducibility and they also indicate the stability of the GC-CAFS technique, whereby even the ultra-trace analytes can always be correctly identified. These chromatographic results serve as a confirmation of the method's capability of managing the complexity of the matrix and providing high-quality, easy-to-understand data [41].

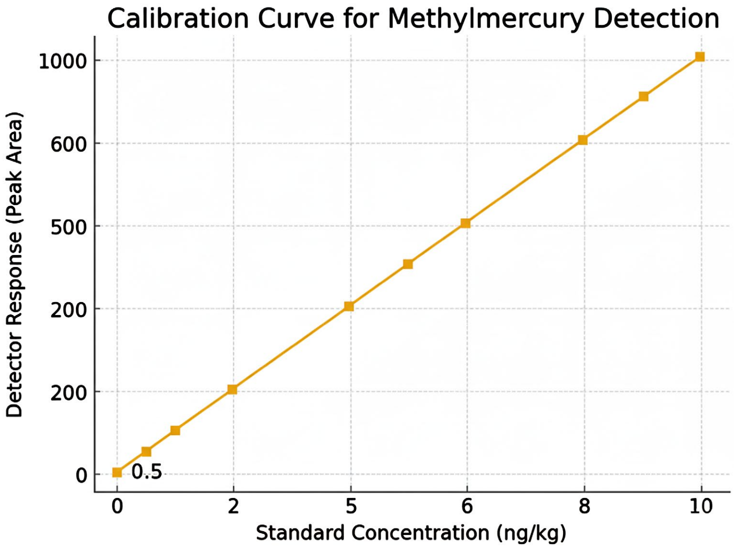


Figure 5. Calibration curve for methylmercury detection.

4.7. Detection Limits and Environmental Relevance

The experiments showed that the system could detect methylmercury at very low concentration levels with detection limits in the nanogram per kilogram (ng/kg) range. This level of sensitivity is especially meaningful in the case of Methylmercury environmental concentrations in soils, which are usually very low but still have a significant ecological impact. Therefore, the detection of even the smallest amounts of methylmercury allows the identification of early contamination signs, which is essential for the environmental management sector to be proactive. This excellent performance of GC-CAFS combined with the use of automated analyzers, provides vital data necessary to make decisions about the level of contamination and plan a safe way of cleaning the polluted area. To this end, the technique is enabling the achievement of the goals set by the international mercury pollution conventions and protocols, e.g., the Minamata Mercury Convention [42].

4.8. Data Processing and Reporting Efficiency

The automatic data processing system was very effective because it offered quick and convenient analysis outputs for example chromatograms, calibration curves, and the concentration values in tabulated form. It did the peak detection as well as peak quantification with almost no manual work. The case of adjustments is replayed here; the working staff are able to make a correct adjustment of the peak boundaries while still having the security of not losing efficiency. In addition, the storage of the analytical results enables the possible comparison of samples collected at different locations and times, thus allowing the study of their development and estimation of their possible risk to the environment. Furthermore, the automatic report function made it possible to quickly and easily output publication-ready formats such as PDFs, thus significantly facilitating the communication of results to stakeholders. These are the benefits that verify the role of automation in environmental monitoring as it considerably diminishes the projects' time and cost, yet is still instrumental in maintaining the same level of data quality.

Figure 6 highlights comparison of analysis time between manual and automated processes highlights significant differences that can impact efficiency and productivity in various laboratory settings. In manual analysis, tasks often involve multiple steps that require direct human intervention, including sample preparation, measurement, data recording, and analysis. Each of these steps consumes time and is subject to variability based on the operator's experience and workflow efficiency. As a result, manual processes can lead to longer analysis times, especially in high-volume environments where repeated actions are required.

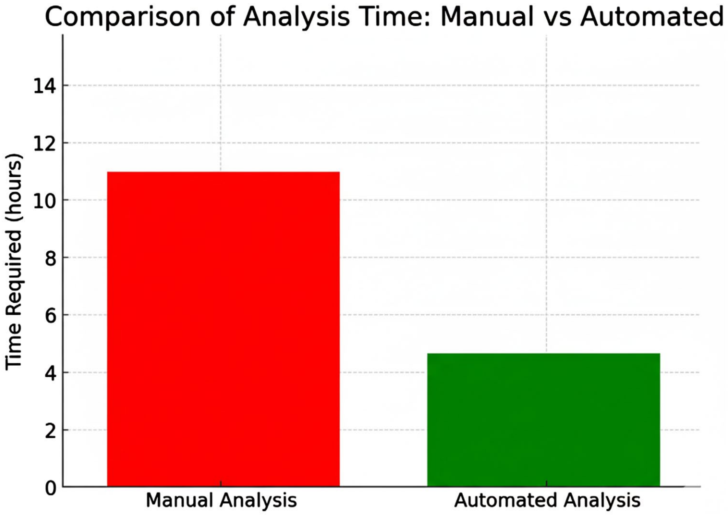


Figure 6. Comparison of analysis time: Manual vs automated.

5. Results and Discussion

And the method was tested on soil samples that were taken at Chemu, Zimbabwe, to illustrate its practical utility. Methylmercury (MeHg) in analysis samples was between 1.8 and 6.3 ng/kg (3.9 ng/kg, n = 9). They are in the lower section of concentrations that are often reported in uncontaminated or slightly contaminated soils, which are often below 10 ng/kg [43]. All samples felt within internationally accepted soil guideline levels of a mercury-contaminated site, which is typically within 10s of µg/kg total mercury [44].

Although these levels are relatively low, the fact that MeHg could be detected is the indicator that its constant monitoring is crucial because even small amounts of this species are bioavailable and can be accumulated in biological food webs on land. The results help prove that the created technique is sensitive enough to catch

MeHg pollution early enough, thus facilitating proactive environmental risk assessment.

Moreover, the lack of range between replicates (RSD < 5) demonstrates the consistency of the technique in thick soil matrices. The measured concentrations are also consistent with the literature on trace MeHg concentrations in soils due to diffuse atmospheric deposition and background geochemical cycling but not acute point-source contamination [45].

In general, these findings indicate analytical performance of the GC-CAFS with automated pre-concentration and the environmental applicability, especially in the evaluation of locations that are potentially at risk of mercury accumulation with industrial or mining processes.

6. Conclusion

The conclusion of this whole analysis is the generation of reports that compile chromatograms, calibration curves, and concentration values. The reporting software provides multiple preview formats, including spectrum curves and summary tables. These reports can either be printed or exported in PDF format, ensuring the high professional standards expected in environmental monitoring studies. The reports comply with the international set standards on the detailing of every aspect of the study. **Figure 4** presents an overview of printed sample reports, which display both raw chromatographic data and processed results. Interpreting the sample chromatogram in light of the concentration curve, and directly linking it to the quantity of pollutants and their levels of concentration in the environment, allows for the quantification, integration, and presentation of the information with a high degree of accuracy.

Limitations and Future Work

Although the resulting method proved sensitive and reproducible, it has a number of limitations. A major difficulty is that humic substances and organic matter in soils can co-elute with methylmercury and reduce detection accuracy due to matrix interference. Despite the effectiveness of pretreatment by distillation to reduce most interferences, trace co-extractives can still interfere. This may be prevented by including more clean-up operations in future work, including selective solid-phase extraction or using thiol-based sorbents to further purify methylmercury species.

The other limitation is that it requires specialized equipment like the analyzer HXAM-51(II) and GC-CAFS which not all laboratories may have due to cost and infrastructure factors. The potential to use alternative detectors such as liquid chromatography with inductively coupled plasma mass spectrometry (LCICP-MS) may also increase access to methylmercury monitoring.

Further studies must also go beyond soils, to include other compartments of the environment like sediments, surface water and biota (e.g. plants and invert animals), because they are also part of mercury cycling and ecological peril. In the long run, monitoring campaigns of mercury affected sites such as in areas around artisanal gold mining or industrial discharge would also enhance insights on methylmercury behavior and guidance on remedial measures.

Having noted these weaknesses and what could be done to enhance the methodology, this study shows that there are some strengths, as well as areas in which research needs to be conducted in order to have a total picture on environmental mercury.

Conflicts of Interest

The authors declare no conflicts of interest.

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