

Microwave digestion and analysis of selected heavy metals in the sediments

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ABSTRACT

The present study focuses on developing an efficient microwave digestion method for the determination of Hg, Cd, and Pb element from water or soil. For the same microwave assisted, digestion method has proposed to solubilize the samples for ICP-MS analysis. At first, sediment samples are air dried, grinded, sieved and subjected to digestion. The digests are subsequently analysed for ICP-MS analysis. Various combinations of acid treatment for microwave assisted digestion method shall be followed. Further, results from ICP-MS analysis of solubilized samples can be compared with Certified Reference material (CRM), Efficacy of the proposed method will be identified.

Key words : Microwave digestion method, CRM, ICP-MS analysis, Hg, Cd, and Pb

Introduction

The main source of environment pollution is due to heavy metal sedimentation which sedimentation has significant effect on ecological balance and its quality (Ettler, 2004). Anthropogenic activities and industrialization often lead to redistribution of abundant heavy metal to different places. Mostly, heavy metal sedimentation at particular place or site will have serious hazardous effect on ecological systems.

Also heavy metals load in sediments, sludges and soils, and through transport, mixing with groundwater and crop cultivation sites, all lead to negative effects on animals and human health (Yuan, 2004). Even after enormous recognized methods for chemical analysis are available, still there is a lack of information or procedure to evaluate low concentrations of heavy metal. For the same, sample size and nature are the limiting factors for

proceeding a successful method. According to available sample analytical methods, physical destruction by dissolution, calcinations or by other digestion methods is quite necessary. In this stage, there must be a loss of the analyses and it will in turn affect accuracy of testing procedure.

For the heavy metal analysis of environmental sediments, the below mentioned common methods are used *viz.*, atomic absorption spectroscopy (FAAS, ETAAS) and inductively coupled plasma-optical emission and mass spectrometry (ICP-OES and ICP-MS). These techniques are selected for their high sensitivity and the main drawback of such techniques is that they require only liquid samples. Most of the sediments are solid in nature and they have to be converted into liquid state for analysis.

The appropriate selection of digestion procedure is mainly based on both the sample nature (presence of organic matter and carbonates), and the analysis

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purpose. Therefore, for heavy metal monitoring of environmental samples for risk assessment, it must be carried out with a great number of samples. The application of acid leaching such as aqua regia and nitric acid may be sufficient. Even though, total digestion procedures shall be included to those samples with heavy metal concentrations close to intervention limits, to avoid the possibility of heavy metal underestimation and ensure the correct decision-making.

Review of Literature

Anthropogenic sources as well as natural contributions *viz.*, volcanic activity and evaporation from the oceans and industrial process have increased Hg levels in the environment. Mercury (Hg) is widely used as a catalyst in manufacturing of sodium hydroxide, gold mining, manufacture of batteries and thermometers, as fungicides, herbicides and disinfectants. It had been characterized as a highly toxic metal among heavy metal deposits around the world. Mercury deposits mainly in sediments and then finally ends up in aquatic systems. Sediments are capable of immobilizing toxic metals but this does not guarantee that the metals are safely removed from aquatic systems. Metals can be reintroduced into the aquatic systems solubility, mobility and bioavailability.

Voica *et al.*, (2011), described about determination of rare earth forms in variety of environmental samples, an important task in generating a fingerprint of the sample, hence the results can be used in determining the origin of the sample. Further, the source of elements that cause environmental pollution could be identified. For surface water samples characterized by a lower degree of pollution, the concentration of rare metals was close to or even below the limit of quantification, then concentrations were considered within the range 0.001-0.5 µg/L (except for Sc 0.5–5 µg/L). Characterization in terms of concentrations of rare metals, comparative water/waters resulting from sediment decantation, revealed that sediments accumulate rare metals

Stefania Gaudino *et al.*, 2007 explained about the measurement of trace-element concentration in soil, sediment and waste. They proposed that a combination of digestion procedure for dissolution of elements and a subsequent measurement of the dissolved elements was beneficial. Either partial or total digestion methods could be used in environmental monitoring activities. In order to determine the

effect of combined methods applied for analysis, measurements from different methods should be compared. Likewise, they reported ICP-MS results obtained after matrix digestion with modified aqua regia (HCl+HNO₃+H₂O₂) method and two “total” digestion methods (microwave aqua regia+HF and HNO₃+HF) results. A comparison report with instrumental neutron activation analysis, a non-destructive analytical method for the determination of the total mass concentrations of inorganic components in environmental matrices was identified by this study.

Reddy *et al.*, (2012), proposed that ICP-MS method is available and adequate to identify and quantify metals present in natural and drinking waters at trace levels, which are of particular relevance for toxicity control regions, may have been contaminated by toxic metals. A number of sophisticated instruments (like ICP-MS, ICP-OES, AAS, UV-VIS spectrometer, Cyclic Voltammetry, etc.) were used for the determination of heavy metals in water. The most effective technique for the determination of trace level contamination of heavy metals in water is ICP-MS and GFAAS. By using ICP-MS (Inductively Coupled Plasma Mass Spectrometry) we can determine up to 0.1µg/L of metal concentration in water.

Methodology

Soil Sample collection

The Samples were collected from Abu Dhabi coastal lines that are from Rom Ghantoot south-west to Abu al Abyad Island and the samples were handled according to the EPA/CE-81-1 protocol and the sediment samples were collected in the Teflon plastic containers.

Acid based microwave digestion method

There were three different Acid based digestion methods namely as A, B and C in the entire three methods two duplicate standard were used and one blank is used in each method.

In method A, which is adopted form Hirata *et al.*, (2006) where the samples are kept in RT for 15 minutes followed by chemical reactive treatment whereas for method B, Ashoka *et al.*, (2009) acid based microwave digestion where the samples are kept in room temperature overnight followed chemical reactive treatment. But in C, (Milestone,

2006) there is no pre-treatment method is followed. In Table 1, there is a list of chemicals that are used in reactive treatment of method A, B and C.

The samples were dried at 110 °C and subject to 4-acid digestion which is in the combination of HCl, Nitric, hydrofluoric and perchloric acids. 1 g of sample (dry weight) was put into a glass beaker, 5 ml H₂SO₄ added and heated to 80 °C. Then, HNO₃ was added and heating continued to 120 °C for 30 min. Next hydrogen peroxide was added until the solution remained clear. Then, the solution was diluted to 100 ml with 2% HNO₃ further microwave acid digestion procedure was optimized with HCl, HNO₃ and in combination of both acids, for the optimization of common reaction condition will be designed to test the efficacy of each procedure as follows, about 0.5 g of sample will be taken and operation pressure was fixed at 200 psi. 65% HNO₃, 40% HF, 37% HCl and 4% H₃BO₃ were the reagents used alone or in mixtures. After cooling, the final solution obtained in digestion procedures was filtered and diluted to 50 mL with doubly distilled water. The obtained digests were stored in polyethylene bottles at 4°C until ICP-MS analysis. After performing ICP-MS analysis of solubilized samples, the outcome results would be compared with CRM. This study could reveal the efficacy of microwave associated acid digestion procedure for ICP-MS analysis. These results are shown in Figure 1(a) and Figure 1(b). The parameters and conditions used for operating the ICP- MS system are explained in flow chart.

Parameters and Conditions in ICP-MS

There is a different parameter that should be considered for operating the ICP-MS system that includes RF power, sample introduction, dwelling time of the sample, total oxygen flow *etc.* and the conditions that were used for this study is listed in Table 1.

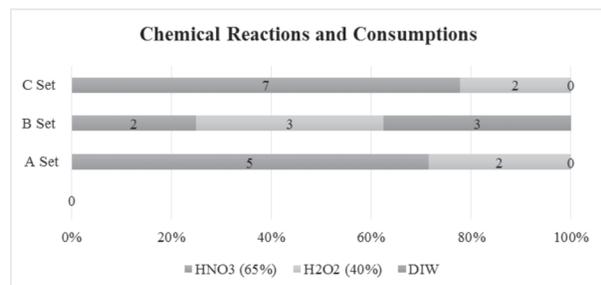


Fig. 1. (a) Chemical Reactions and Consumptions of the soil sample

Total reactive volume (mL)

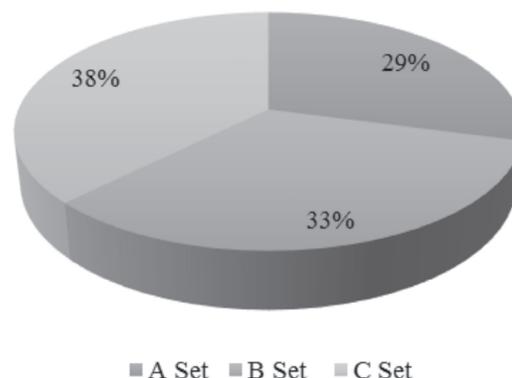


Fig. 1. (b) Total reaction volume of the given sample

There were three different acid based microwave digestions used in sample which was divided into

Table 1. Different acid based digestion method using for analysing the soil sample.

Method	HNO ₃ (65%) Reactive volume (mL)	H ₂ O ₂ (40%) Reactive volume (mL)	DIW	Total reactive volume (mL)
A Set	5	2	0	7
B Set	2	3	3	8
C Set	7	2	0	9

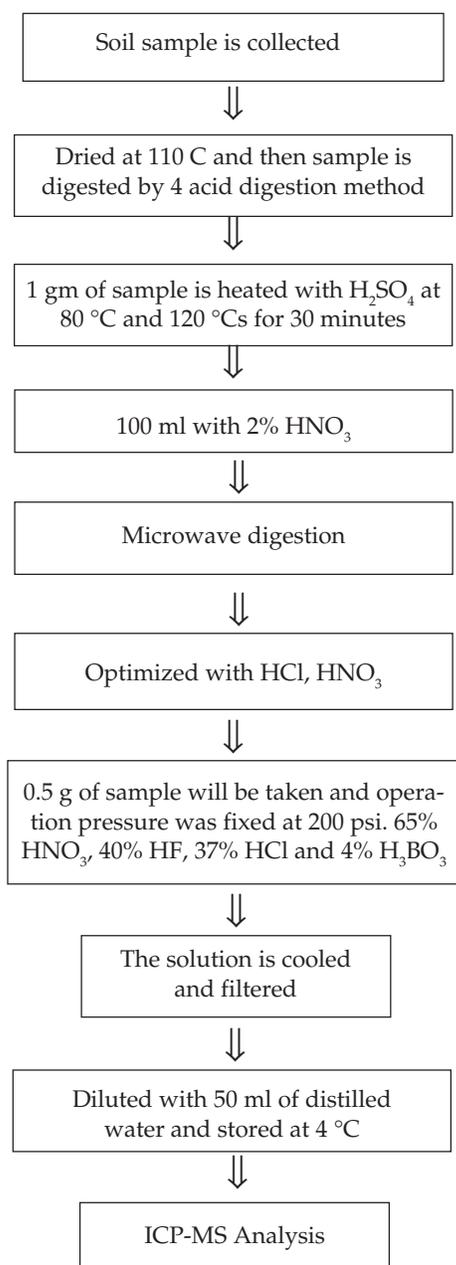
three sets and different ICP-MS operating conditions were used which is listed in Table 2. The results of different operation conditions used for three different acid based microwave digestion are filled in the Table 3.

The results that are obtained from the above table is used to show the difference between the operational conditions for 3 different sets of MD method

Table 2. Conditions and parameters for ICP-MS

ICP-MS parameter	Conditions for operating the instrument
Sample introduction	Meinhard nebulizer
Spray chamber	Cyclonic spray chamber
RF power	1500 w
Injector	Alumina
Monitored ion m/z	91 (75As16O) and 103(Rh) for DRC
Total acquisition time	600 Ms
Dwell time	700 sec
Oxygen flow for DRC	0.24 mL/min

The parameters and conditions used for operating the ICP-MS system



in % in Figure 2: (a) and in psi for Figure 2: (b).

Certified reference material (CRM)

In the present study, the results of the sediment analysis are compared with the CRM sample that consist of contains certified values of 60 elements including Hg, Cd, and Pb, obtained from the mean of 14 independent laboratories, provided by the In-

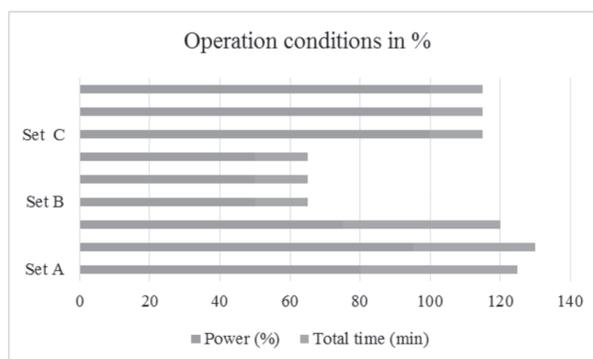


Fig. 2. (a) Operational conditions for 3 different sets of MD method in %

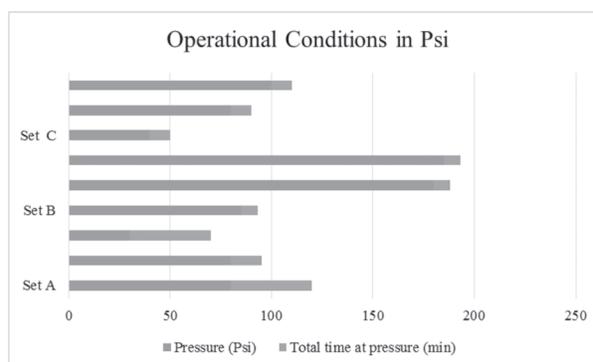


Fig. 2. (b) Operational conditions for 3 different sets of MD method in Psi

stitute of Geophysical and Geochemical Exploration. The certification process of this CRM was verified by 7 other external expert laboratories.

Statistical Analysis and Results

The statistical analysis was carried out on three different sample methods and two ways ANOVA analysis was carried out to determine the significant difference with a 95% confidence interval. The analysis was carried out using SPSS 15 software.

Concentration of the Hg, Pb and Cd in soil samples using different acid based microwave method

Recovery percentage from the Hg, Cd, and Pb of the microwave digested sample that consist of the sample sets under different microwave digested conditions is shown in Fig. 3. The percent recovery of Hg, Cd, and Pb from the microwave digested sample from three set A, B, C (2 ways ANOVA) and the concentration of the Hg, Pd and Cd in soil samples from Abu Dhabi Coastline using different acid based microwave method is shown in Table 4.

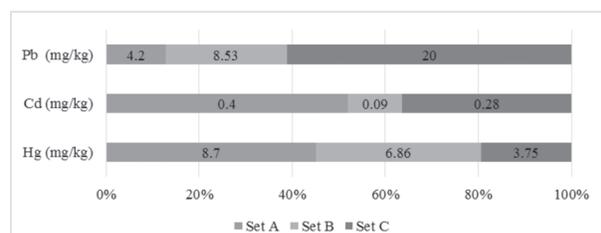


Fig. 3. The percent recovery of Hg, Cd, and Pb from the microwave digested sample from three set A, B, C (2 ways ANOVA)

Three different acid based microwave digestion methods namely A, B and C were used in this study. In set A, the concentration of Hg, Cd and Pb was observed to be 8.70, 6.86 and 3.75 mg/kg whereas in Set B was found to have lower concentration of Hg, Cd and Pd when it was compared to Set A and C. the concentration of set C was found to be significant highest when compared to set A and B. the concentration of Pb was significantly high when compared to the concentration of the Pb concentration in set A and B. Pb concentration of set C was 20 mg/kg is the highest concentration when compared to other compound such as Hg and Cd when compared to all the three methods.

Comparison of CRM samples using different acid based microwave digestion validation methods:

There was a significant difference when compared to set A and B was compared with set C. However,

there was a slight difference was observed between the set B between the Hg, Cd, and Pb digestion, but there was no significant difference observed from the sedimentation sample.

The Table 5 shows the different sediment CRM validation values results and the recovery element are represented in mg/kg, there was no significant difference observed between the SD values of the three different elements and there was no much difference between the microwave validation values between A and B that is represented in mg/kg. The concentration of the Pb in set C was significantly highest when compared to Pb concentration of other set A and B. The concentration of Pb of Set C was 18.33 mg/kg whereas the concentration of Pb in set B was found to at its lowest with a concentration of 0.25 mg/kg. The graphical representation of CRM

Table 5. Validation results showing the percent recovery and of Hg, Cd and Pb from the soil sediment CRM and the optimized value of acid based microwave digestion method

Analyte	Microwave digestion validation results of CRM sample		
	Hg	Cd	Pb
SET A*	6.70 ± 0.50	8.86 ± 0.29	2.85 ± 0.12
SET B*	0.45 ± 0.009	0.07 ± 0.001	0.25 ± 0.010
SET C*	2.20 ± 0.10	6.53 ± 1.15	18.33 ± 3.08

*Sediment CRM: NCSDC 74482 (coastal deposits)

Table 3. Different operation conditions used for three different acid based microwave digestion method.

	Stage	Power (%)	Total time (min)	Pressure (Psi)	Total time at pressure (min)
Set A	1	80	45	80	40
	2	95	35	80	15
	3	75	45	30	40
Set B	1	50	15	85	8
	2	50	15	180	8
	3	50	15	185	8
Set C	1	100	15	40	10
	2	100	15	80	10
	3	100	15	100	10

Table 4. Concentration of the Hg, Pd and Cd in soil samples from Abu Dhabi Coastline using different acid based microwave method

Sample	Hg (mg/kg±SD)	Cd (mg/kg±SD)	Pb (mg/kg±SD)
Set A	8.70 ± 0.65	0.40 ± 0.008	4.20 ± 0.40
Set B	6.86 ± 0.27	0.09 ± 0.003	8.53 ± 2.25
Set C	3.75 ± 0.16	0.28 ± 0.014	20 ± 4.05

samples using different validation method (Set A, B and C) are shown in Figure 4.

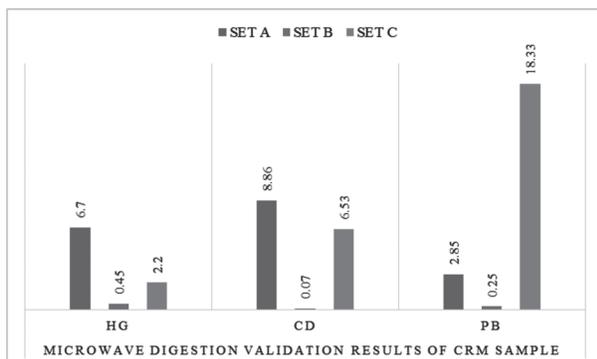


Fig. 4. Graph represents the CRM samples using different validation method (Set A, B and C)

Comparison of Hg with CRM Samples and Coastline Samples

In Figure 5, the Hg concentration from two different samples is compared with different method A, B and C. The Hg value from Set A of both CRM sample and from the coastline showed the highest concentrations followed by Set B and C. Set B was found to have lowest concentration of Hg from both CRM and coastline samples which was significant when compared to set A samples. However, Set B and C were not significant when compared from both the samples. In Table 6 it shows the comparison of Hg with CRM Samples and Coastline Samples with all 3 sets.

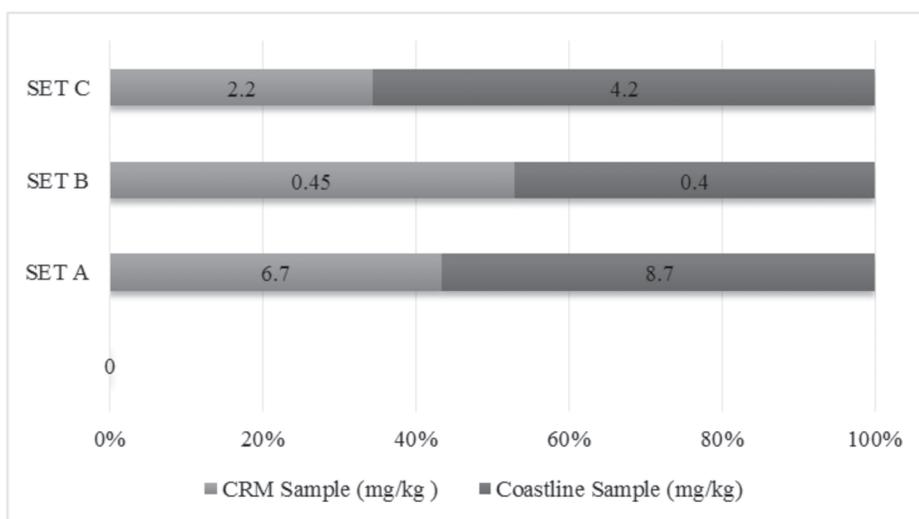


Fig. 5. Graph showing the comparison of Hg of Sets A, B and C with coastline and CRM sample (t-test)

Comparison of Cd with CRM Sample and Coastline Sample

In Figure 6, the Cd concentration of two different samples was compared with three different acid based microwave digestion methods. The set C the concentration of Cd was found to be significant from both CRM and coastline samples whereas in Set B the concentration of the Cd was found to be the lowest is significant compared to set C of both

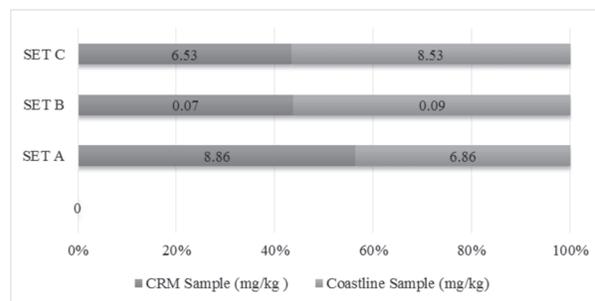


Fig. 6. Graph showing the comparison of Cd of method A, B and with coastline and CRM (T-test) sample

Table 6. Comparison of Hg with CRM Samples and Coastline Samples with all 3 sets

Compound	CRM Sample (mg/kg)	Coastline Sample (mg/kg)
SET A	6.7	8.7
SET B	0.45	0.4
SET C	2.2	4.2

the samples. Table 7 shows the Comparison of Cd with CRM Sample and Coastline Sample.

Table 7. Comparison of Cd with CRM Sample and Coastline Sample

Compound	CRM Sample (mg/kg)	Coastline Sample (mg/kg)
		Cd
SET A	8.86	6.86
SET B	0.07	0.09
SET C	6.53	8.53

Comparison of Pb with CRM Sample and Coastline Sample

Pb concentration from the Set C from both the sample was found to the highest when compared to set A and B. where the concentration of the Pb was found to be lowest in Set B of both the samples shown in Figure 7. Table 8 shows the comparison of Pb with CRM Sample and Coastline Sample.

Comparison of CRM samples with the Samples from the marine coastline

In Figure 8, the two samples are compared with

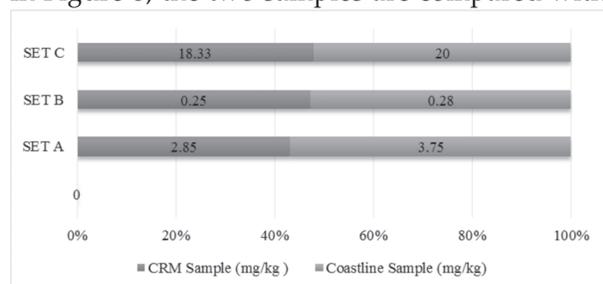


Fig. 7. Graph showing the comparison of Pb of method A, B and with coastline and CRM (T-test)

Table 8. Comparison of Pb with CRM Sample and Coastline Sample

Compound	CRM Sample (mg/kg)	Coastline Sample (mg/kg)
		Pb
SET A	2.85	3.75
SET B	0.25	0.28
SET C	18.33	20

three different acid based microwave digestion method named as set A, B and C. The set C of both the sample are found to be significant when compared to Set B of CRM and coastline samples. The Set B showed the lowest concentration of Hg, Cd and Pb of both the samples which is followed by Set A. The Set A and B of both the samples where compared which was not significant. Table 9 shows the comparison of CRM samples with the Samples from the marine coastline.

Detection limit

The minimum detection method was used to detect the minimum level of Hg, Cd and Pb by using the new acid based digestion method. The values are 1.443 µg/L for Hg, 1.234 µg/L for Cd and Pb was 0.033. However, the instrument detected values as 1.501 µg/L for Hg, 1.200 µg/L for Cd and Pb to be 0.004.

Discussion

In this study, the soil samples collected from the Abu Dhabi coastal lines were collected and evaluated. In this study, three different acid digestion

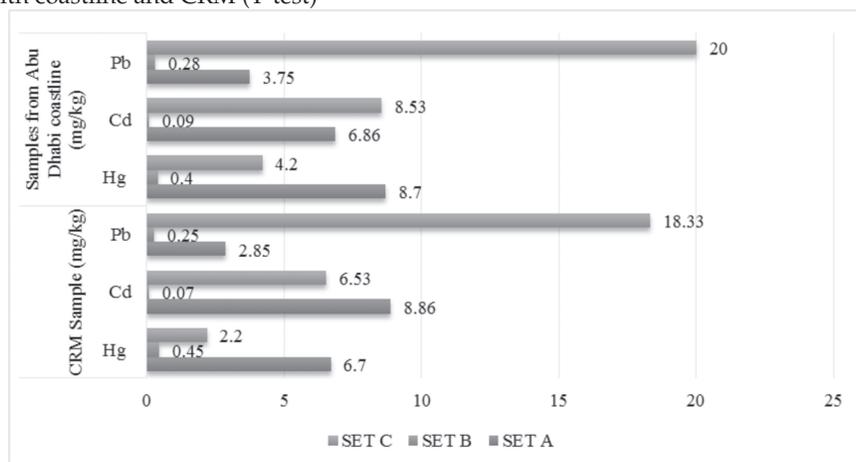


Fig. 8. Graph showing comparison of CRM sample with samples from Abu Dhabi coastline using three different Acids based microwave digestion method (ANOVA analysis)

Table 9. Comparison of CRM samples with the Samples from the marine coastline

Compound	CRM Sample (mg/kg)			Samples from Abu Dhabi coastline (mg/kg)		
	Hg	Cd	Pb	Hg	Cd	Pb
SET A	6.7	8.86	2.85	8.7	6.86	3.75
SET B	0.45	0.07	0.25	0.4	0.09	0.28
SET C	2.2	6.53	18.33	4.2	8.53	20

methods were utilized which is compared to the CRM soil sample which is treated with different acid based digestion method. The CRM samples is compared to the coastline soil sample to validate which method is more efficient and sensitive in detecting heavy metals such as Hg, Cd and Pb in both the samples.

Kazemi *et al.*, (2011) have reported the concentration of the heavy metal concentration in the coastal zone of Arabian Gulf of Pb to be around 0.61–6.48 ppm and the concentration of cd in soil sample to be around 5.99–37.66 ppm. In this study, the samples collected from the Abu Dhabi coastline, the concentration of the Hd, Cd and Pd was estimated to be around 2.85, 0.25 and 18.33 mg/ kg which was analysed by using ICP-MS analysis and these values were compared to CRM (Certified Reference Material) samples where the values of Hg, Cd and Pd was found to be around 0.40, 0.09 and 26 mg/kg respectively which showed higher concentration when C method (Milestone, 2006) was used where the samples subjected to 65% HNO₃ and 40% H₂O₂ treatment which was found to be efficient and sensitive in detecting the heavy metals in the sample followed by ICP-MS analysis where different operation conditions were used (Table 2). The Set B showed the least amount of the concentration in both the samples, this may be due to inefficiency or less sensitivity in detecting heavy metals such as Hg, Cd and Pb. In this study as shown in the Figure 4 and 5, the concentration of the Pb was found to be the highest in the both the soil sedimentation samples. Moreover, Pb concentration is found to high in concentrations in polluted soil. The sample was treated and analysed using ICP-MS instrumentation, especially near the Industrial area.

Cd is found to be in lower concentration after Pd where the highest concentration was found in the both CRM and Abu Dhabi coastline samples of set A and C respectively. The set A CRM sample contained about 8.86 mg/kg whereas the set c of coastline sample contained about 5.53 mg/kg concentration of Cd. Cd heavy metal is associated with the

marine coastline pollution. The Cd metal can be absorbed by the soil or with other compounds such as Fe, Mn or humic acid. The Cd absorption into the soil can influence the ionicity of the water and Cd carbonates into the sediment that could affect the pH. Higher concentration of Cd is related to the pollution of the heavy metals. The marine fishes and soil can contain high concentration of the heavy metals which is indirectly associated with the soil found in the coastlines where the fishes can contain high concentration of heavy metals such as Hg, Cd and Pb which are to be hazardous when it is used as food for human consumption.

In figure % graph reveals that the overall Hg concentration is low when it is compared to the other compound that is digested by using different acidic based microwave digestion method. Hg can remain stable with organic matter (Liu *et al.*, 2003) where is can be transmitted to marine organism and Hg remains stable. At the end of the study, it can be concluded that set C method was the most efficient method for detecting heavy metal pollution. Where the sample is digested with 65% HNO₃ and 40% H₂O₂, the sample is not pre-treated before chemical reaction treatment.

Conclusion

There are several studies that have been carried out to obtain the most accurate and efficient method for the extraction of the metals which is later subjected to ICP-MS method. The main benefit of using acid based extraction is that the whole method is less time consuming when compared to other methods and most importantly there is less uptake of acid into the sample which results in more accurate extraction and yields more accurate reading. Moreover, this Acid based microwave digestion method is more valid as this method is compared with CRM samples. In these methods, the recovery of the metals was efficient to carry out further analysis. High concentration of heavy metals in coastline can determine the marine pollution in the sea which affects

both the marine organism and humans. Analysis of soil sedimentation can be used as an indicator for monitoring the aquatic pollution. Heavy metals such as Hg, Cd and Pb can easily combine with the coast water where the metals integrates with the Geo-chemical cycle and the metals will enter the marine organism and become hazardous and can affect the humans indirectly. Therefore, further studies should be carried out by using more number of samples from different locations.

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