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The Suitability of Digestion Techniques in the Assessment of Certain Metals in Standard Reference Materials

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ABSTRACT

The assessment of various digestion methods is of utmost importance in accurately determining the concentrations of elemental metals in soil. In this study, the dry digestion method utilizing a graphite furnace oven was compared to the wet digestion method employing a microwave. Four standard reference materials, namely Randwijk clay, Hengelo sandy soil, Halle sandy soil, and Herveld clay samples, were subjected to analysis using an inductively coupled plasma optical emission spectrometer (ICP-OES). The reliability of the data obtained was ensured by calculating the recovery and error percentage of the results for both digestion methods. The findings indicate that the microwave digestion method is superior for all elements in soil samples, except for calcium, chromium, and magnesium. On the other hand, the dry digestion method may be favored for calcium, copper, chromium, magnesium, sodium, nickel, and vanadium. A pair t-test statistical analysis was conducted to compare the two methods, revealing significant differences, except for calcium, chromium, copper, iron, potassium, and sodium, indicating a lack of agreement between the two methods, except for these specific elements.

Keywords: Dry digestion, Microwave digestion, Standard Reference Material, ICP/OES.

INTRODUCTION

Acidic digestion procedures are employed to convert solid samples into liquid extracts, facilitating the quantification of overall or pseudototal concentrations of metallic elements in soils. This crucial process involves the release of metals from the solid matrix into the acidic solution during extraction. Such procedures are essential for the determination of metals using conventional techniques like inductively coupled plasma optical emission spectrometry or atomic absorption spectroscopy.[1]

Numerous acid digestion methods have been documented in the literature for the analysis of heavy metals in soils. These methods encompass a wide range, from mild attacks, such as aqua regia in an open system, to the utilization of hydrofluoric acid in a closed system, which is considered a complete digestion method for the breakdown of silicate matrices[2]. The digestion of samples stands as a major contributor to the uncertainty surrounding analytical results, owing to the significant variations in metal content obtained through different methods[3-6]. To ensure the comparability of data, it is imperative for regulatory agencies to standardize the method employed for determining metal concentrations in soils.

Dlamini *et al. ,*[7] presented the optimization, validation, and application of microwave-assisted digestion and inductively coupled plasma mass spectrometry (ICP-MS) for the simultaneous determination of trace metals [boron (B), cadmium, cobalt, chromium, copper, molybdenum, nickel, lead, selenium, vanadium, zinc, and arsenic] in soils from sludgeland.

Naicker *et al.,*[8] described the analysis of twelve trace elements in soil and sediment samples using microwave-assisted and ultrasonic-assisted digestion prior to analysis with inductively coupled plasma optical emission spectroscopy. Agnieszka, *et al.,*[9] conducted a study in which they presented the findings of their investigation into the measurement of heavy metal concentration in soil. They employed two distinct methods for adding soil components into solution and utilized different laboratory techniques and types of measuring equipment. The first method utilized was the hot digestion of soil samples with a mixture of concentrated HNO_3 and $HClO_4$, following the prior ashing of organic matter (referred to as the IUNG method). The second method involved a two-stage decomposition process, whereby soil samples were initially hot digested with an oxidizing acid (HNO_3) and subsequently with a non-oxidizing acid (HF) (referred to as the two-stage decomposition method). The concentrations of selected heavy metals (Cr, Cu, Fe, Mn, Ni, Pb, and Zn) were determined in solutions obtained through both digestion methods.

The aim of this investigation is to assess the efficacy of two digestion methods, specifically the dry digestion method and the wet digestion method, in the determination of heavy metals in four standard reference materials.

MATERIALS AND METHODS

The development of the digestion methods and the analysis of four certified reference materials (CRMs), namely clays and sandy soil, were undertaken. HCl and HNO_3 were analytical grade reagents and were used as received.

Samples

Four certified reference materials (CRMs) were procured for the purpose of this study. The specific details of these samples are provided below (Table 1).

Two digestion methods were utilized, namely graphite furnace digestion (dry ashing) and microwave digestion, as outlined by Greenberg *et al.,*[10].

Table 1: Sampledetails

Sample No	Type	Country
1	Clay from river basin	Randwijk/Netherland
2	Sandy soil	Hengelo/Netherland
3	Sandy soil	Halle/Netherland
4	Clay	Herveld/Netherland

Dry digestion

A quantity of 1.00 g of each CRM was weighed and placed into a 30 mL porcelain crucible. The crucible was then introduced into a muffle furnace and gradually heated to a temperature of 700°C, allowing the sample to ashed for a duration of 4 hours. Following this, the crucible was carefully removed and cooled in a desiccator, as described by Chattopadhyay *et al.,*[11].

Subsequently, 10 mL of Aqua regia solution (consisting of a 3:1 v/v ratio of HCl to HNO_3) were added to the cooled ash and stirred until dissolved. Any undissolved fraction was allowed to precipitate and then filtered into a 25 mL volumetric flask. The resulting solution was diluted with deionized water to a final volume of 50 mL.

Microwave Digestion

For this method, a mass of 0.2 g of each sample was weighed and placed into a microwave Teflon vessel. The vessel, along with the sample, was inserted into the HTC safety shield. Subsequently, 3.8 mL of HNO_3(65%), 5 mL of HCl (37%), 1 mL of HF 40%, and 5 mL of H_3BO_3 5% were added to the Teflon vessel. The vessel was then sealed and inserted into the rotor segment, which was in turn introduced into the microwave cavity and connected to the temperature sensor. The total digestion method was loaded and, upon completion of the program, the rotor was cooled using water until the solution reached room temperature. The vessel was then opened and the solution transferred into a 100 mL volumetric flask, following the protocol outlined by Ahmed *et al.,*[12].

Sample Analysis

The prepared samples from section 2 were subjected to analysis using inductively coupled plasma optical emission spectrometry (ICP/OES), employing the specified operational conditions showed in Table 2.

Table 2: ICP-OES 725 E Operating conditions

Parameter	Setting
Power	1.2 KW
Plasma flow	15 L/min
Aux. Flow	1.5 L/min
Neb. Flow	0.75 L/min
Replicate read time(s)	10 Sec.
Sample Uptake time	30 Sec.
Rinse Time	25 S
Pump rate	15 rpm
Instrumental stabilization delay	15 S

RESULTS AND DISCUSSION

The accurate determination of heavy metals in soils holds significant importance in the process of remediation of contaminated soils and the monitoring of land application of nonhazardous materials containing metals. Prior to the measurement of metal concentrations in soils, sample digestion is often required[13].

Quality control of the two digestion methods

In general, the microwave digestion method applied to all four SRMs yielded accurate results (80-120% Recovery) for all elements, except for Mg and Cr in the Hengelo sandy soil and Herveld clay samples[14].

In comparison to microwave digestion, the dry digestion method demonstrated accurate results for Ca, Cu, K, Mg, Na, and V in the Randwijk clay sample (Table 3), Na, Ni, and V in the Hengelo sandy soil (Table 4), Cr and Cu in the Halle sandy soil (Table 5), and Cu in the Herveld clay.

Table 3: Analysis of Randwijk clay sample

		Method A: Dry digestion		
Element	Analytical value	Certified value	Recovery%	Error%
Ca	8391.75	7964	105.36	5.4
Cr	133.458	98.3	135.76	35.77
Cu	23.9816	24.98	109	4
Fe	42183.76	33470	126	26
K	17197.8	19409	88.5	11.4
Mg	7837.023	7185	109	9
Mn	1626.026	1244	130	30.7
Na	5258.705	6315	83.27	16.7
Ni	55.23023	43.62	126.6	26.6
V	75.45993	92.63	81	18
Zn	140.8378	105.5	133	33
		Method B: Microwave digestion		
Element	Analytical value	Certified value	Recovery%	Error%
Ca	6484	7964	81.4	18.6
Cr	82.639	98.3	84.1	15.9
Cu	21.522	24.98	86.2	13.8
Fe	39324	33470	117.5	17.4
k	20807.2	19409	107.2	7.2
Mg	7294.99	7185	101.5	1.5
Mn	1430	1244	114.9	14.9
Na	5815	6315	92.1	7.9
Ni	38.34	43.62	87.9	12.1
V	84.16	92.63	90.9	9.1
Zn	86.9	105.5	82.4	17.6

From the data presented in Table 3, it can be observed that method A, also known as the Dry digestion method, exhibits favorable outcomes in terms of recovery and error percentage for the elements Ca, Cu, K, Mg, Na, and V. Conversely, it demonstrates unsatisfactory recovery and high error rates for the remaining elements. On the other hand, method B, referred to as the Microwave digestion method, demonstrates commendable recovery and acceptable error rates for all the elements under investigation. Analyzing the dry digestion of the Hengleo soil sample, as illustrated in Table 4, it becomes evident that the dry digestion method proves to be effective in terms of recovery and acceptable error only for Na, Ni, and V. Conversely, the microwave digestion method exhibits satisfactory recovery and error rates for all the elements being studied, with the exception of Mg.

Table 5 presents the quality control outcomes for the Halle sandy soil sample. It is evident from method A that the dry digestion method in the Halle sandy soil sample yields favorable recovery and error rates only for Cr and Cu. In contrast, the microwave digestion method (Method B) demonstrates good recovery and error rates for all the elements under investigation. For the Herveld clay sample, the quality control results are displayed in Table 6. In this case, the dry digestion method (method A) exhibits satisfactory recovery and error rates solely for Ca and Cu. On the other hand, the microwave digestion method (method B) demonstrates good recovery and error rates for all the elements under scrutiny, with the exception of Cr and Mg.

Overall, the quality control results for both the dry digestion method and the microwave digestion method indicate that the latter offers superior recovery and error rates. The ashing process in the dry digestion method is challenging to regulate and presents the potential for uneven heating and cross-contamination of samples[15].

Table 4: Analysis of a sandy soil sample obtained from Hengelo

Method A: Dry digestion

Element	Analytical value	Certified value	Recovery%	Error%
Ca	1629.72	1238	131.6	31.6
Cr	24.572	36.06	68.1	31.8
Cu	11.9733	8.424	142.133	42.13
Fe	3091.59	2541	121.6	21.6
K	3930.79	6382	61.5	38.4
Mg	498.404	339.7	146.7	46.7
Mn	93.7402	75.93	123.4	23.4
Na	2019.75	2262	89.2	10.7
Ni	11.6374	11.5	101.1	1.2
V	12.5985	11.17	112.7	12.8
Zn	25.407	19.35	131.3	31.3

Method B: Microwave digestion

Element	Analytical value	Certified value	Recovery%	Error%
Ca	1322	1238	106.7	6.9
Cr	37.066	36.06	102.8	2.8
Cu	7.88	8.424	93.5	6.5
Fe	2740	2541	107.8	7.8
K	6283.27	6382	98.5	1.5
Mg	245.915	339.7	72.4	27.6
Mn	68.16	75.93	89.8	10.2
Na	1922	2262	85	15
Ni	12.9	11.5	112.2	12.2
V	10.37	11.17	92.8	7.1
Zn	21.16	19.35	109.4	9.3

Table 5: Analysis of Halle sandy soil sample

Method A: Dry digestion

Element	Analytical value	Certified value	Recovery%	Error%
Ca	2876.87	2038	141.2	41.8
Cr	53.4526	45.69	116.9	16.9
Cu	12.2088	12.58	97	2.9
Fe	5362.1	3972	135	35
K	6489.39	8848	73.3	26.7
Mg	709.971	505.9	140.3	40.3
Mn	315.745	231.1	136.6	36.6
Na	2835.9	3710	76.4	23.6
Ni	11.1007	8.008	138.75	38.75
V	39.6215	26.83	147.7	47.7
Zn	37.6768	30.33	124.2	24.2

Method B: Microwave digestion

Element	Analytical value	Certified value	Recovery%	Error%
Ca	1960	2038	96.1	3.8
Cr	42.509	45.69	93	6.9
Cu	11.732	12.58	93.2	6.7
Fe	4307	3972	108.4	8.4
K	8487.72	8848	95.9	4.1
Mg	407.893	505.9	80.6	19.4
Mn	232.9	231.1	100.8	0.7
Na	3149	3710	84.9	15.1
Ni	8.444	8.008	105.4	5.4
V	24.42	26.83	91	8.9
Zn	27.84	30.33	91.8	8.2

Table 6:Analysis of Herveld clay sample

Method A: Dry digestion

Element	Analytical value	Certified value	Recovery%	Error%
Ca	3886.53	4030	96.4	3.6
Cr	58.73899	79.91	73.1	26.9
Cu	16.24053	13.8	117.4	17.4
Fe	14545.17	19380	75.1	24.9
K	10711.5	15895	67.4	32.6
Mg	1926.547	3070	62.7	37.2
Mn	404.6386	603.1	67.1	32.9
Na	4731.833	6985	67.7	32.3
Ni	12.76765	19.58	65.2	34.8
V	32.19403	51.55	62.4	37.5
Zn	91.21643	123	74.1	25.9

Method B: Microwave digestion

Element	Analytical value	Certified value	Recovery%	Error%
Ca	3549	4030	88.1	11.9
Cr	59.308	79.91	74.2	25.8
Cu	12.289	13.8	89	11
Fe	19520.9	19380	100.7	0.7
K	14186.53	15895	89.3	10.7
Mg	2326.479	3070	75.8	24.2
Mn	598.5	603.1	99.2	0.76
Na	6021	6985	86.2	13.8
Ni	19.37	19.58	98.9	1.1
V	48.15	51.55	93.4	6.6
Zn	107.1	123	87.1	12.9

Comparison between the dry and microwave digestion methods

To conduct a comparison between the dry digestion and microwave digestion methods employed for the preparation of four Standard Reference Materials (SRMs) in order to determine the concentration of eleven elements using Inductively Coupled Plasma Optical Emission Spectrometry (ICP/OES), a paired t-test was used. The paired t-test was implemented using the equations provided by Shigeki Tsuneya *et al.,*[16], denoted as equation 1 and equation 2.

$$T = \frac{\bar{d}}{SE(\bar{d})} \qquad (1)$$

$$SE(\bar{d}) = \frac{Sd}{\sqrt{n}} \qquad (2)$$

Where: T represents the calculated t-value, d represents the mean difference, Sd represents the standard deviation of the difference, SE(d) represents the standard error of the mean difference, and N represents the number of readings.

Consequently, the paired t-test results for the dry and microwave digestion methods were obtained for the four SRMs using equations 1 and 2. These results were then tabulated in Tables 7-10, which display a comparison between the dry and microwave digestion methods.

Table 7: Randwijk clay sample comparing the dry and microwave digestion methods by mean of paired t-test

Element	Difference (µg/g)	standard deviation (µg/g)	SEof the mean difference	Calculated t
Ca	5907.75	4983.218	1502.497	-0.38129
Cr	1050.819	4500.089	1356.828	-0.42222
Cu	215.4596	4954.276	1493.77	-0.38351
Fe	2859.76	5212.005	1571.479	-0.36455
K	-13609.4	5355.932	1614.874	-0.35475
Mg	542.032	2850.27	859.3888	-0.66661
Mn	1196.026	3077.201	927.811	-0.61745
Na	-4556.3	3342.704	1007.863	-0.56841
Ni	46.89023	2708.525	816.651	-0.7015
V	-8.70007	3054.849	921.0715	-0.62197
Zn	53.9378	3574.414	1077.726	-0.53156
	$\bar{d}$=-572.88			

As demonstrated in Table 7, and based on the tabulated values for the two-sided t-distribution, the values for $t_{0.05}$ (t=1.8) and $t_{0.025}$ (t=2.2) exhibit no significant disparity. This indicates that both procedures are in concurrence with one another.

Table 8: Hengelo sandy soil sample comparing dry and wet digestion by mean of paired t-test

Element	Difference(µg/g)	standard deviation(µg/g)	SEof the meandifference	Calculated t
Ca	707.7238	840.9866	253.567	-0.07477
Cr	-12.494	806.0094	243.021	-0.07801
Cu	16.09332	849.23	256.0525	-0.07404
Fe	351.587	899.8386	271.3116	-0.06988
K	-2352.48	944.4462	284.7612	-0.06658
Mg	952.4885	355.1257	107.0744	-0.17706
Mn	25.58015	41.45191	12.49822	-1.5169
Na	97.74583	8940.762	2695.741	-0.00703
Ni	-1.26257	8947.76	2697.851	-0.00703
V	2.228467	8947.618	2697.808	-0.00703
Zn	4.246995	10617.98	3201.443	-0.00592
	$\bar{d}$=-18.96			

As depicted in Table 8, and based on the tabulated values for the t-distribution with two tails, it can be observed that for $t_{0.05}$ (t=1.8) and $t_{0.025}$ (t=2.2), there is no statistically significant difference between any of the elements. This implies that both methods are in agreement with each other.

Table 9: Comparison between dry and wet digestion of Halle sandy soil, utilizing the paired t-test as the statistical measure

Element	Difference(µg/g)	Standard deviation(µg/g)	SEof the meandifference	Calculated t
Ca	21916.87	8475.886	2555.576	1.497961
Cr	10.94358	6012.146	1812.73	2.111816
Cu	0.476819	6291.67	1897.01	2.017993
Fe	19055.1	6613.085	1993.92	1.919912
K	-3998.33	2611.752	787.4727	4.861314
Mg	4422.078	1974.002	595.184	6.43188
Mn	632.8446	1539.768	464.2575	8.245752
Na	-313.101	1549.149	467.0861	8.195818
Ni	18.65667	1515.711	457.0042	8.376623
V	15.20146	1513.387	456.3034	8.389489
Zn	348.9279	1622.398	489.1713	7.82579
	$\bar{d}$=3828.15			

As evidenced by the data presented in Table 9 and the corresponding values for the two-sided t-distribution, it is noteworthy that $t_{0.05}$ (t=1.8) and $t_{0.025}$ (t=2.2) exhibit statistically significant disparities across all variables, with the exception of Ca. This discrepancy implies that the two methods employed do not concur, except in relation to Ca.

Table 10: Herveld clay sample comparing dry and wet digestion by mean of paired t-test

Element	Difference(µg/g)	Standard deviation(µg/g)	SEof the mean difference	Calculated t
Ca	337.5301	2294.337	691.7686	-0.94701
Cr	-28.569	2270.791	684.6691	-0.95683
Cu	42.95153	2380.47	717.7387	-0.91275
Fe	2592.265	2504.446	755.1188	-0.86756
K	-6475.03	2279.051	687.1597	-0.95337
Mg	-399.932	1028.625	310.1421	-2.1123
Mn	-293.861	1121.838	338.247	-1.93679
Na	-2889.17	1238.549	373.4366	-1.75428
Ni	-10.6024	313.1411	94.41561	-6.93862
V	-15.956	355.4829	107.1821	-6.11216
Zn	-65.8836	416.6489	125.6244	-5.21486
	$\bar{d}$=-655.11			

As presented in Table 10, and according to the tabulated values for the two-sided t-distribution, it is observed that for $t_{0.05}$ (t=1.8) and $t_{0.025}$ (t=2.2), all elements exhibit significant differences, except for Ca, Cr, Cu, Fe, K, and Na. This implies that the two methods do not agree with each other, except in the case of Ca, Cr, Cu, Fe, K, and Na.

Turek *et al.,*[17], conducted an investigation on various digestion procedures, namely drying and microwave digestion, ignition and microwave digestion, and drying and conventional digestion, for the purpose of evaluating heavy metal content in sludge samples. The results obtained indicate that the most effective method was ignition and microwave digestion.

Microwave-assisted and ultrasonic-assisted digestion techniques were applied prior to analysis using inductively coupled plasma optical emission spectroscopy, as described by Naicker *et al.,*[8]. The authors concluded that both digestion methods yielded similar levels of accuracy, suggesting their suitability for precise determination of the target metals. Dlamini *et al.,*[7] validated the microwave assisted digestion method for determining heavy metal concentrations in soil from sludge land, using ICP/MS. Their conclusion indicates that all validated parameters fell within acceptable limits, indicating the suitability of the method for its intended purpose. Abegunde *et al.,*[18] conducted a study comparing three conventional acid digestion procedures for soil samples. Their findings revealed that the behavior of each metal towards the digestion acid can guide the selection of the appropriate digestion procedure. In an inter-laboratory study carried out by Santoro *et al.,*[19], different digestion methods were employed for a sewage sludge certified reference material. The results obtained demonstrated no significant differences between the extraction methods used. Two digestion techniques were compared and applied to real soil samples and standard reference materials for the analysis of Sb using ICP/MS. The recoveries of Sb achieved through HF in the acid digestion mixture in a closed-vessel microwave digestion system were found to be excellent, and the concentrations obtained were in very good agreement with certified or reported concentrations of reference materials. Monlau *et al.,*[21] focused their study on anaerobic digestion with pyrolysis in soil. The results obtained indicated that both solid-digestate and pyrochar exhibited favorable properties as soil amendments, albeit with complementary effects.

CONCLUSION

The comparison of dry digestion method and wet digestion method show that the microwave digestion method was superior for analyzing all elements in soil samples, except for calcium, chromium, and magnesium. On the other hand, the dry digestion method is recommended for the analysis of calcium, copper, chromium, magnesium, sodium, nickel, and vanadium base on the present study. Based on the obtained results, the conclusion is drawn that microwave digestion is suitable for sample preparation for various soil types, including soil, sandy soil, and clay samples.The microwave digestion method is recommended for use in determining heavy metal concentrations in soil and river basin samples. This recommendation suggests that the microwave digestion method is reliable and effective for preparing samples and extraction of heavy metal content in environmental samples.

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Conflicts of Interest

The author declare(s) that there is no conflict of interest regarding the publication of this paper.

REFERENCES

1. Da Silva, Y.J.A.B.; do Nascimento, C.W.A. & Biondi, C.M. Comparison of USEPA, digestion methods to heavy metals in soil samples. *Environ Monit Assess.*, **2014,** *186*, 47–53 https://doi.org/10.1007/s10661-013-3354-5.
2. Chen, M.; Ma, L. Q., & Harris, W. Comparison of four USEPA digestion methods for trace metal analysis using certified and Florida soils. *Journal of Environmental Quality.*, **1989**, *27*, 1294–1300.
3. Kántor, T. Electrothermal vaporization and laser ablation sample introduction for flame and plasma spectrometric analysis of solid and solution samples. *Spectrochimica Acta Part B: Atomic Spectroscopy.*, **2001**, *56*, 1523–1563.
4. Axelsson, M., & Rodushkin, I. Determination of major and trace elements in sphalerite using laser ablation double focusing sector field ICP-MS. *Journal of Geochemical Exploration.*, **2001**, *72*, 81–89.
5. Belarra, M. A.; Resano, M.; Vanhaecke, F., & Moens, L. Direct solid sampling with electrothermal vaporization/atomization: what for and how? TrAC *Trends in Analytical Chemistry,* **2002**, *21*, 828–839.
6. Al-Harahsheh, M.; Kingman, S.; Somerield, C., & Ababneh, F. Microwave-assisted total digestion of sulphide ores for multi-element analysis. *Analytica Chimica Acta.*, **2009**, *638*, 101–105.
7. Hlengiwe Dlamini, Precious Mahlambi& Sihle Mngadi Validation of microwave-assisted digestion and Inductive coupled plasma-mass spectrometer for the determination of trace metals in the soil around Darvillsludgeland and their environmental complications, *Soil and Sediment Contamination.*, **2023**, *32*(6), 637-651, DOI: 10.1080/15320383.2022.2123446
8. Kavisha Naicker, Precious Mahlambi & Mphilisi Mahlambi Comparison of ultrasonic and microwave assisted digestion methods for the determination of heavy metals in soil and sediment: The effect of seasonal variations on metal concentrations and risk assessment, *Soil and Sediment Contamination.*, **2023**, *32*(3), 320-336, DOI: 10.1080/15320383.2022.2084032.

9. Operacz.; Agnieszka.; Adrianna Bigaj.; Karolina Hap, and Tomasz Kotowski. "The Effect of Sample Preparation and Measurement Techniques on Heavy Metals Concentrations in Soil: Case Study from Kraków, Poland, Europe" *Applied Sciences*., **2022**, *12*(4), 2137-2141. https://doi.org/10.3390/app12042137.
10. Isabel Greenberg.; Anja Sawallisch.; Jan Stelling.; Michael Vohland.; Bernard Ludwig.; Optimization of sample preparation and data evaluation techniques for $\bar{X}$ ray fluorescence prediction of soil texture, pH, and cation exchange capacity of loess soils, *Soil Science Society of America Journal*., **2023**, 1-16 https://doi.org/10.1002/saj2.20598.
11. Chattopadhyay, P.; Fisher, A.; Henon, D. Matrix Digestion of Soil and Sediment Samples for Extraction of Lead, Cadmium and Antimony and Their Direct Determination by Inductively Coupled Plasma-Mass Spectrometry and Atomic Emission Spectrometry. *Microchim. Acta*., **2004**, *144*, 277–283. https://doi.org/10.1007/s00604-003-0113-2.
12. Ahmed, A.Y.; Abdullah, M.P. &Siddeeg, S.M.Environmental hazard assessment of metals in marine sediments of Sabah and Sarawak, *Malaysia. Int. J. Environ. Sci. Technol*., **2023**, *20*, 7877–7886. https://doi.org/10.1007/s13762-022-04514-z.
13. Mingtao Xiang.; Yan Li.; Jiayu Yang.; Kaige Lei.; Yi Li.; Feng Li.; Daofu Zheng.; Xiaoqian Fang.; Yu Cao.; Heavy metal contamination risk assessment and correlation analysis of heavy metal contents in soil and crops, *Environmental Pollution*., **2021**, *278*, 1169-1180. https://doi.org/10.1016/j.envpol.2021.116911.
14. Xi Zhong.; Ziwu Chen.; Yaying Li.; Kengbo Ding.; Wenshen Liu.; Ye Liu.; Yongqiang Yuan.; Miaoyue Zhang.; Alan J M Baker.; Wenjun Yang.; Yingheng Fei.; Yujie Wang.; Yuanqing Chao.; Rongliang Qiu.; Factors influencing heavy metal availability and risk assessment of soils at typical metal mines in Eastern China, *Journal of Hazardous Materials*., **2020**, *400*, 22-32. https://10.1016/j.jhazmat.2020.123289.
15. Soylak, M.; Tuzen, M.; Narin, I.; and Sari, H. Comparison of microwave, dry and wet digestion procedures for the determination of trace metal contents in spice samples produced in Turkey," *Journal of Food and Drug Analysis*., **2004**, *12*(3), 254-258 https://doi.org/10.38212/2224-6614.2634.
16. Shigeki Tsuneya.; Makoto Nakajima.; Yohsuke Makino.; Suguru Torimitsu.; Rutsuko Yamaguchi.; Hirotaro Iwase.; A quantitative comparison between using sodium hypochlorite as a digestion method for the diatom test and the conventional method using fuming nitric acid, *Forensic Science International*., **2021**, *329*, 86-111. https://doi.org/10.1016/j.forsciint.2021.111086.
17. Turek.; Anna.; Kinga Wieczorek, and Wojciech M. Wolf., Digestion Procedure and Determination of Heavy Metals in Sewage Sludge-An Analytical Problem" *Sustainability*, **2019**, *11*(6), 17-53. https://doi.org/10.3390/su11061753
18. Abegunde S. M.; Oyebanji A. O.; Osibanjo O.M.; Evaluation of Digestion Procedures on Heavy Metals in Soil of a Dumpsite in Ibadan, South-western Nigeria, *Suan Sunandha Scienceand Technology Journal*., **2018**, *5*(2), 1-5 10.14456/ssstj.2018.6.
19. Anna Santoro.; Andrea Held.; Thomas P.J. Linsinger.; Andres Perez.; Marina Ricci. Comparison of total and aqua regia extractability of heavy metals in sewage sludge: The case study of a certified reference material, *TrAC Trends in Analytical Chemistry*., **2017**, *89*, 34-40, https://doi.org/10.1016/j.trac.2017.01.010.
20. Amereih, S.; Meisel, T.; &Wegsheider, W.; Accurate Determination of Total Antimony Using ICP-MS and Optimization Its Extraction Efficiency From Reference and Soil Samples. *Palestine Technical University Research Journal*., **2018**, *6*(1), 48–58. https://doi.org/10.53671/pturj.v6i1.56.
21. Monlau F.; Francavilla M.; Sambusiti C.; Antoniou N., Solhy A., Libutti A., Zabaniotou A., Barakat A., Monteleone M., Toward a functional integration of anaerobic digestion and pyrolysis for sustainable resource management. Comparison between solid-digestate and its derived pyrochar as soil amendment, *Applied Energy*., **2016**, *169*, 652-662. https://doi.org/10.1016/j.