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DETERMINATION OF HEAVY METALS IN SOIL AND SEDIMENT USING VARIOUS MICROWAVE DIGESTION TECHNIQES

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ABSTRACT

The objective of the current research is to examine eight different digestion methods to accurately determine seven trace elements (Cd, Co, Cr, Cu, Pb, Ni and Zn) in soil and sediment samples by inductively coupled plasma-mass spectrometry (ICP-MS). The performance of these methods were evaluated by applying four Proficiency Testing (PT) samples received from the Canadian Association for Environmental Analytical Laboratories (CAEAL) in January 2007 round, through the accreditation program (ISO 17025).

In order to validate the accuracy of the selected techniques, another four PT soil samples of June 2007 round and a certified reference material (CRM 2703) were applied. The results of this validation process showed that the selected methods are confirmed to be ideal for the accurate determination of these heavy metals in soil samples.

The overall results enable any laboratory to develop certified values for certain standard reference material based on these recommended methods, and consequently make them available to the various laboratory and customers. In addition it can assist scientists, worldwide, to choose the most appropriate technique for analyzing trace-metal concentrations in soils and sediments.

KEYWORDS: ISO 17025, soil and sediment analysis, heavy metals, microwave digestor, Proficiency Test, ICP-MS, CRM 2703.

INTRODUCTION

The accurate chemical analysis of heavy metals in soil and sediment samples receives lots of attention from the scientific community due to its role as indicators for soil/plant environmental status. Therefore, a necessity to apply a rapid and accurate determination of heavy metals in soil has led to the development of various analytical methods concerning both the sample digestion and the choice of appropriate instrumental technique.

Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) is a very powerful technique for the simultaneous determination of trace elements with very low detection limits and linear calibration curves over five orders of magnitude (Hassan, *et al.*, 2007). The very low detection limits claimed for ICP-MS can only be reached when the concentration of total dissolved solids in the solution to be analyzed is kept to a minimum. Sample digestion is often a necessary step before the analysis of metal in soils with highly sensitive spectroscopic techniques (Hassan, *et al.*, 2007, Lo and Sakamoto, 2005; Sandroni *et al.*, 2003; Chen and Ma, 2001).

Microwave-assisted technique is recognized as a more convenient, reproducible, accurate, and less time-consuming method than conventional digestions on hot plates. Due to the necessity of demand of precise and consistent analytical results, the digestion parameters (mass of sample,

digestion mixture, temperature and power/time steps) should be optimized and controlled during the digestion. Moreover, for the purpose of achieving the goal of total decomposition, the use of acid combinations for the digestion are also considered very critical (Mico *et al.*, 2007; Hassan *et al.*, 2007; Gaudino *et al.*, 2007; Melaku *et al.*, 2005; Sun *et al.*, 2001; Marr *et al.*, 1995)

The digestion method strongly influences the accuracy of the result depending on the type of sample and acids used for digestion (EPA, 1996; 1998). For example, the nitric acid procedure was reported to be the most efficient in the determination of Cd, Mn, and Ni from composite samples. The Aqua regia digestion might give close results for the maximum levels of polluting metals such as Cd, Cu, Pb, and Zn in soils (Marr et al., 1995), while metals like Ba, Cr, and Ni could be efficiently recovered only by using HF digestion (Sawhney and Stilwell, 1994). For geochemical analysis, Rantala and Loring (1989) recommended the use of an aqua regia-HF combination for removing total metals in marine sediments, while Lo and Sakamoto (2005) proved that the HNO_3-HF mixture showed better efficiency than aqua regia-HF mixture for marine sediment. Thus, great elemental recovery should be sought during selection.

Digestion procedure could be the source of uncertainty and contamination due to incomplete mineralization of the organic matter, formation of volatile compounds and atmospheric contamination. Therefore, it is crucial to evaluate the acid digestion protocol for an accurate determination of metals content in soil sample. Therefore this paper is aimed to evaluate eight acid digestion mixtures for the determination of Cd, Cr, Co, Cu, Pb, Ni and Zn in soil and sediment.

METHODOLOGY

Proficiency testing (PT) is an internationally recognized method of checking analytical laboratory testing performance by means of inter-laboratory test. A series of PT samples is periodically submitted by CAEAL to participants for the determination of a range of heavy metals, with the results generated being assessed statistically by a quantitative method that is consistent with ISO/IEC Guide 43-1 and the internal Harmonized Protocol for Proficiency Testing of (Chemical) Analytical Laboratories (1997).

The various experiments, conducted within the current study, were performed to establish routine methods for soil/sediment digestion using eight digestion mixtures for PT soil and sediment samples.

1- Equipments

1-1- Microwave assisted acid digestor

Digestion of soil samples was performed using a Milestone (Socisole, Italy) Model MLS-1200 MEGA Microwave Digestion System, with a rotor for 10 Teflon digestion vessels designed for pressure up to 30 bars, served as closed-pressurized microwave system. These vessels are equipped with a pressure release system to prevent explosions. The operating frequency of microwave system was 2450 MHz and the power range of the oven could be set in 10 W increments up to a maximum of 1000 W.

1-2- Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

The ICP-MS, Perkin-Elmer model ELAN 9000 was used for the determination of total metal (Cd, Cr, Co, Cu, Pb, Ni and Zn), coupled with autosampler AS-93 plus. The standard

operating conditions were followed during the analyses and listed in table (1). These condition were optimized daily prior to the analysis.

2- Reagents and Standards

Multielement standard solutions containing 1000µg ml^{-1} of tested element were obtained from Merck (Darmstadt, Germany). High-purity water was obtained from Milli-Q system (Millipore, France) with electrical resistivity of 18.2 MΩ cm. All acids (HNO_3, HCl, HF, H_2O_2 and $HClO_4$) used in the experiments, were analyzed to determine levels of metals impurity.

3-Digestion Procedures

3-1- Acid digesting reagents

Five different acids were used with various ratios. Nitric acid (HNO3, 65%), perchloric acid (HClO4, 70%) and Hydrogen peroxide (H_2O_2, 50%) were used as powerful oxidizing agents. The oxidizing power of $HClO_4$ is proportional to its concentration and temperature. Therefore, due to its extremely rapid reactivity with organic matrices, $HClO_4$ was mixed with HNO_3. This combination of acids allows for a controllable digestion of organics. Hydrochloric acid (HCl, 35%) was used in combination with other acids for dissolution of metals. Hydrofluoric acid (HF, 40%) was used to break silicate bonds. Eight-digested mixtures were used for PT (January, 2007 round) samples as follows:

Method 1: HNO3 + HF + H_2O_2 (1:1:1)
Method 2: HNO_3 +H_2O_2 (2:1)
Method 3: HNO_3 + HCl (3:1)
Method 4: HNO_3 + $HClO_4$ + H_2O_2 (5:1:1)
Method 5: HNO_3 + HCl + H_2O_2 (2:1:0.08)
Method 6: HNO3 + HCl + HF (3:0.5:1)
Method 7: HNO_3 + HCl (1:3)
Method 8: HNO3 + HCl + HF (1:3:1.3)

3-2- PT and CRM Sample preparation

To test the analytical performance of the digestion methods employed, eight PT samples and CRM 2703 were used in this study. The four PT samples were received from CAEAL in January and June 2007 rounds through the accreditation program (ISO 17025) of CLEQM. A Certified reference material (CRM 2703) from the National Institute of Standard and Technology (NIST) was used for validating the accuracy of the overall analytical procedures

The samples were prepared by accurately weighing 0.1g of sample into the microwave digestion vessels. The eight acid mixtures were added separately to the vessel. Blanks were prepared with the same procedures. The sample solutions and the blanks were digested in microwave at 175±5^{0}C. For good reproducibility of the results, the digestion conditions (temperature, pressure and duration of digestion) were kept constant for all procedures. The solution was cooled, then filtered and transferred to 100 ml volumetric flasks. Each solution was diluted to 100 ml with deionized water. Duplicate digestions were carried out.

4- Quality Control / Quality Assurance

Metal concentrations in the extract were determined following CAEAL-approved Quality Assurance Plan. All calibration curves for trace metals had a correlation coefficient of R ≥0.998. Quality assurance samples (blank, duplicate and reference material) were analyzed for every run. Quality-control samples (analytical blanks and calibration standards) were included in the determination of elemental concentrations in the digestion solution using an ICP-MS.

5- Performance Evaluation

Two statistical analyses were applied to analyze the performance of the eight digested acids procedures.

5-1- Recovery Calculation

Accuracy was determined by comparing the measured concentration with the PT designed values reported by CAEAL and was expressed as percentage recovery (% R). Calculation of the recovery of each metal was based on the certified value [measured concentration/Assign value (μg/g)×100]. Based on the Environmental Protection approved research quality assurance plan (Chen and Ma, 2001), satisfactory accuracy was required to be within 80% (Lower Recovery Limit, LRL) to 120% (Upper Recovery Limit, URL) for all elements, which corresponded to the uncertainty of the NIST-certified values, according to a 95% confidence interval for the true values
.

5-2- CAEAL Evaluation

ISO Guide 43-1 gives two basic measures for evaluating the result of proficiency testing, the normalized error (E_n-value) and the z-score. CAEAL considers the z-score approach as the most useful and meaningful for chemical or biological analysis. Specifically, z-score measures the deviation from the designed value in a certain way that allows comparison with the performance criteria as follows:

5-2-1- z-score

The performance of the different investigated procedures was evaluated utilizing the z-Score approach as follows:

$$z = (x_{Lab} - X^*_{assigned}) / s^*_{Population}$$

Where

x_{lab} = reported result by the individual laboratory;
$X^*_{assigned}$ = assigned value;
$(x_{Lab} - X^*_{assigned})$ = deviation from the assigned value; and
$s^*_{Population}$ = assigned standard deviation

5-2-2- Composite PT score:

Since each PT round involves four separate samples of distinct concentration for each test, it is necessary to calculate a composite PT score for each test to determine the overall performance. The composite (or PT) score based on the Lab's results for all valid samples is considered acceptable if it is equal or greater than 70% at z score equal 2 s*.

RESULTS AND DISCUSSION

The determination of trace metals in soil and sediment samples has gained in importance during the past decades (Hassan, et al 2007, Lo and Sakamoto, 2005). Concentrations of toxic and essential elements in such samples provide valuable information about the trace element status and can be the basis of appropriate treatment investigation. The current section is mainly concerned with presenting the various results produced from the different chemical analyses associated with their discussion.

Accuracy of the digestion methods in analyzing elements in PT samples

Evaluation of digestion methods is necessary to assure that reliable results and conclusions are obtained. The evaluation process was carried out using the result of January 2007 PT soil/sediment samples supplied by CAEAL in order to check data quality. Two scenarios were applied on the resulting data.

1-Evaluation of elemental recoveries

The results of different acid combination were compared to the designed values of PT sample (January, 2007 round) reported by CAEAL. Table (2) indicates the accuracy (as recovery percentage) of eight digestion procedures for the determination of seven elements in four PT soil samples.

1-1- Cadmium

Figure 1 shows the accuracy (as mean percentage recovery) results of cadmium digestion by the eight investigation methods in the four PT samples. Presented results show that methods (4, 7 and 8) give percentage of recovery ranged between (84-102%), (84-93%) and (100-117%) respectively with the four PT samples. The results indicate that these three methods are suitable for Cd determination in soil matrix. This result is due to the aqua regia used in both methods 7 and 8, which was strongly recommended by Chen and Ma (2001) and for digestion of diverse samples attributed to its complete digestion performance and good recoveries. The percentage recovery of Cd from this PT type of soil using method 3 ranged between (63-98), indicted that further investigation using different type of soils is needed.

1-2- Chromium

Figure 2 shows the mean recovery percentage results of chromium digestion by the eight investigation methods. Presented results show that both methods 1 and 3 give satisfactory results (107-117%) and (90-110%) respectively for all sample concentrations. The HNO_3-HF mixture in method 1 was found to completely decompose a high-carbon ferrochromium metallurgical sample under a microwave-heating program. The capacity of this mixture is due to the low boiling points and large partial pressure of HNO_3 and HF. The pressure inside the vessel is greatly increased as the temperature is increased; thus, complete or nearly complete dissolution was attained. Method 2 (70-106%) needs extensive study. Method 4 (HNO_3+ $HClO_4$+H_2O_2) gives satisfactory result with high concentration only (108%). This is due to perchloric acid that rises to $^{40}Ar^{37}Cl^{+}$ which interfered with the lower concentration of Cr with ICP-MS at the same m/z. Analytical difficulty and low recoveries of four chromium concentrations by microwave-based aqua regia+ HF are obtained although the mean recovery is satisfactory. These results are consistent with what has been reported by Chen and Ma (1998).

1-3- Cobalt

Figure 3 shows the mean recovery percentage results of cobalt digestion by the eight investigation methods. Results show that both methods 3 and 4 give recovery ranges (75-126%) and (113-150%); with an overall satisfactory result (94 and 119%) respectively. High concentrations of PT samples are recovered by both methods 2 and 5. Aqua Regia (method 7) indicates satisfactory average result of (112%) except for the second PT sample (140%), which can be reasoned to the great complexity of the dissolved matrix.

1-4- Copper

Figure 4 shows the copper digestion results of the eight investigation methods. Accordingly, these results indicate that method 3 gives good results with a satisfactory recovery except the second PT sample (128%), which can be reasoned to the great complexity of the dissolved matrix. High concentrations were recovered using methods 2, 7 and 8. Further investigation with respect to Cu analysis is needed.

1-5- Lead

Figure 5 shows the results of lead digestion by the eight experimental methods. Lead was satisfactory recovered by methods 3 and 4. Methods 1, 2 and 7 give satisfactory with high concentration samples.

1-6- Nickel

Results for the eight experimental methods of nickel are presented in figure 6, regarding the recovery percentage. These results show that Nickel was recovered by method 1 (HNO_3+ HF+H_2O_2) but incomplete dissolution of Ni (<80%) mineral was obtained for the second PT sample, which implies that Ni in this soil may be present as insoluble minerals. It was noticed that high concentration was recovered by methods 2, 3 and 7.

1-7- Zinc

Figure 7 shows the zinc digestion result of the eight methods. Accurate results were obtained for all zinc concentrations in all methods except 6 and 7(Aqua Regia). However, method 8 (Aqua regia+ HF) gives good recovery (102%).

2- CAEAL Evaluation:

Tables 3-9 indicate the method performance according to the ISO/IEC Guide 43-1 (1997). This method evaluation is subject to the criterion that when composite PT score records ≥70% using any method, this method is considered satisfactory.

It was clearly observed from the results that cadmium could be accurately determined using methods 4, 7 and 8. Chromium gives satisfactory PT results with four samples in methods 1 and 3, while Cr composite PT score was satisfactory with method 2. The composite PT score of cobalt give satisfactory results (>70%) using methods 3,4 and 7. Nickel concentration can be measured with aqua regia and method 3 in high concentration and method 1 needs more investigation. Zinc gives satisfactory results with all methods except 6 and 7. Methods 3 and 4 give good results in measuring lead, while method 3 for copper needs more trails to pass PT test according to CAEAL evaluation.

3- Validation of the selected methods

In order to assess the applicability and compatibility of the selected four-digestion method (3, 4, 7, and 8), standard reference material (CRM 2703) and four PT samples of another round (June 2007) were used for validating the accuracy of the overall analytical procedures. The most suitable combination of acids used for the digestion was applied. The analytical results, shown in figures 8-14, indicate that the concentration of all investigated elements, determined by ICP-MS, were in agreement with the CRM 2703 and PT sample (June 20007 round) designed values.

Conclusion and Recommendation

The current research was mainly concerned with developing internationally accepted and reliable chemical procedures for the determination of heavy metals in soil and sediment. Microwave digestion techniques were developed to determine the content of seven heavy metals (Cd, Co, Cr. Cu, Pb, Ni, and Zn) in sediments and soils. The digests were subsequently analyzed by ICP-MS. The method performance is evaluated quantitatively by QC procedure that is consistent with ISO/IEC Guide 43-1 and the International Harmonized Protocol for PT of Analytical Laboratories.

Precise analysis was achieved for all elements by method 3 mixture (HNO_3+HCl). This combination produced the most accurate analytical results for the PT samples provided by CAEAL in January 2007 round, with a recovery of 88–107% and a precision better than 5%. On the other hand, the combinations applied in methods 4 (HNO_3 +$HClO_4$+H_2O_2), method 7 (aqua regia) and method 8 (aqua regia +HF) showed high accuracy in determining certain specific elements.

In order to assess the applicability and compatibility of the selected four digestion method (3, 4, 7, and 8), another four PT soil samples provided by CAEAL in June 2007 round and a certified reference material (CRM 2703) were used for validating the accuracy of these procedures. The results of this validation process showed that these four methods are confirmed to be ideal for the accurate determination of these heavy metals in soil samples.

The overall results, produced within the current manuscript, enable any laboratory to develop certified values for certain standard reference material based on these recommended methods, and consequently make them available to the various users and customers. In addition it can assist scientists, worldwide, to choose the most appropriate technique for analyzing trace-metal concentrations in soils.

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Table 1: Operating conditions for the ICP-MS

Plasma	RF power	Forward 1300 Watts
Argon gas flow	Auxiliary gas	1.2 L min^{-1}
	Nebulizer gas	0.92 L min^{-1}
Nebulization		Type: cross flow Uptake ≈ 1.5 ml min^{-1}
Ion sampling	*Sample cone*	Platinum mounted on a nickel base, orifice 1.1 mm diameter
	Skimmer cone	Platinum mounted on a nickel base, orifice 0.9 mm diameter

Table 2: Mean percentage recovery (%) of metals in Proficiency Test (PT) soil /sediment of January, 2007 applying eight acid digestion mixtures

Metals	Digestion Methods							
	1	2	3	4	5	6	7	8
Cd	255.82	174.63	75.433	93.089	136.11	275.31	88.401	105.38
Cr	112.6	85.3	103.4	127.5	20.9	96.7	73.6	105.04
Co	146.8	123.7	93.8	119.1	137.95	204.6	112.6	123.88
Cu	183.3	292.4	106.5	178.0	0	0	255.67	122.61
Pb	142.6	140.9	87.4	108.6	201.3	198.0	119.58	174.1
Ni	91.6	63.1	91.4	160.3	150.1	163.6	143.14	165.5
Zn	96.6	91.8	104.1	102	104.5	123.5	0	101.9

Table 3: Determination of Cadmium in PT soil samples (January 2007 round) by selected digestion methods according to CAEAL evaluation

PT Code Cadmium	Design Value	s	Digestion Methods								
			4			7			8		
			Reported.	z	point	Reported.	z	point	Reported	z	point
C17-1	1.71	0.19	1.739	0.15	97.75	1.58	0.684	89.737	1.71	0	100
C17-2	1.75	0.2	1.489	1.303	80.46	1.48	1.35	79.75	1.75	0	100
C17-3	3.04	0.28	3.092	0.186	97.21	2.82	0.786	88.214	3.55	1.82	72.7
C17-4	3.72	0.34	3.12	1.765	73.53	3.12	1.765	73.529	3.89	0.5	92.5
PT Score					87.24			82.808			91.3

Table 4: Determination of Chromium in PT soil samples (January 2007 round) by selected digestion methods according to CAEAL evaluation

PT Code Chromium	Design value	S	Digestion Methods								
			1			2			3		
			Reported.	Z	point	Reported	z	point	Reported	z	point
C17-1	53.4	5.97	58	0.77	88.5	50.6	0.47	92.9	58	0.77	88.4
C17-2	52.7	6.36	56.6	0.61	90.8	56.1	0.52	92.1	57.7	0.79	88.2
C17-3	71.3	7.53	84	1.68	74.8	50.1	2.82	57.7	74.8	0.46	93
C17-4	77.1	8.25	89.9	1.55	76.7	53.9	2.81	57.9	69.7	0.89	86.6
PT score					82.7			75.2			89.1

Table 5: Determination of Cobalt in PT soil samples (January 2007 round) by selected digestion methods according to CAEAL evaluation

PT code Cobalt	Design	s	Digestion methods								
			3			4			7		
			Rep	Z	point	Rep	Z	point	Rep	Z	point
C17-1	37.8	3.76	34.4	0.9	86.4	42.75	1.33	80.06	40.43	0.713	89.309
C17-2	9.56	0.98	12.1	2.62	60.7	9.83	0.276	95.87	13.39	3.908	41.378
C17-3	13.6	1.42	11.3	1.65	75.2	14.9	0.915	86.27	14.24	0.451	93.239
C17-4	12.4	1.39	9.24	2.26	66.1	18.6	4.475	32.88	12.21	0.122	98.165
PT					72.1			73.77			80.523

Table (6): Determination of Copper in PT soil samples (January 2007 round) by selected digestion methods according to CAEAL evaluation

PT code Copper	Design	s	Method		
			3 *		
			Reported	Z	point
C17-1	540	37.4	461	2.11	68.3
C17-2	38.9	2.85	50	3.91	41.3
C17-3	76	5.85	91	2.57	61.5
C17-4	75.1	5.63	69.1	1.07	84
PT					63.8

*Method 3 needs further investigation

Table 7: Determination of Lead in PT soil samples (January 2007 round) by selected digestion methods according to CAEAL evaluation

PT code Lead	Design	s	Methods								
			3			4			7*		
			Reported	z	point	Reported	z	point	Reported	z	point
C17-1	47.4	3.92	47.2	0.05	99.2	55.02	1.952	70.73	56.42	2.309	65.37
C17-2	47	3.66	47	0.01	99.9	50	0.822	87.66	69	6.014	9.7951
C17-3	162	11.8	125	3.13	53	180	1.536	76.96	180.5	1.574	76.391
C17-4	223	17.1	163	3.52	47.2	225.8	0.158	97.63	225	0.11	98.35
PT					74.8			83.25			62.476

* Method 7 needs further investigation

Table 8: Determination of Nickel in PT soil samples (January 2007 round) by selected digestion methods according to CAEAL evaluation

PT Code Nickel	Design	s	Method		
			1*		
			Reported	Z	point assigned
C17-1	814	95.2	1058	2.56	61.5
C17-2	37.8	3.37	27.7	2.99	55.2
C17-3	53.4	5.56	48.3	0.9	86.5
C17-4	47	5.02	34.2	2.55	61.8
PT score					66.3

*Method 1 needs more investigation

Table 9: Determination of Zinc in PT soil samples (January 2007 round) by selected digestion methods according to CAEAL evaluation

PT Code Zinc	Design	s	Methods								
			1			2			3		
			Reported	Z	point	Reported	Z	point	Reported	Z	point
C17-1	748	54	795	0.88	86.8	688	1.1	83.5	676	1.33	80
C17-2	222	18.3	168	2.97	55.4	160	3.41	48.9	288	3.59	46.2
C17-3	1532	127	1559	0.21	96.8	1549	0.13	98.1	1504	0.22	96.7
C17-4	1328	109	1379	0.47	93	1357	0.27	96	1298	0.28	95.9
PT					83			81.6			79.7
			Methods								
			4			5			8		
Code	Design	s	Reported	Z	point	Reported	Z	point	Reported	Z	point
C17-1	748	54	768	0.373	94.4	785	0.696	89.6	711	0.68	89.8
C17-2	222	18.3	238.8	0.895	86.57	223	0.019	99.7	252	1.62	75.7
C17-3	1532	127	1670	1.08	83.8	1571	0.303	95.5	1547	0.12	98.2
C17-4	1328	109	1183	1.334	79.99	1465	1.257	81.1	1307	0.19	97.1
PT					86.19			91.5			90.2

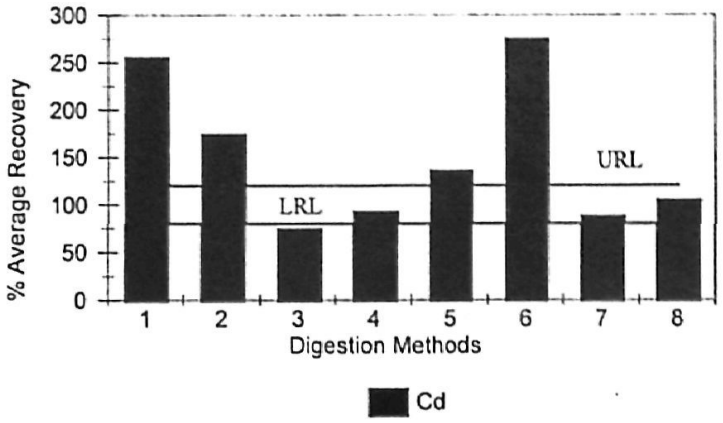

Fig 1: Recovery percentages of cadmium with different acid digestion solutions; (URL: Upper Recovery Limit, LRL: Lower Recovery Limit)

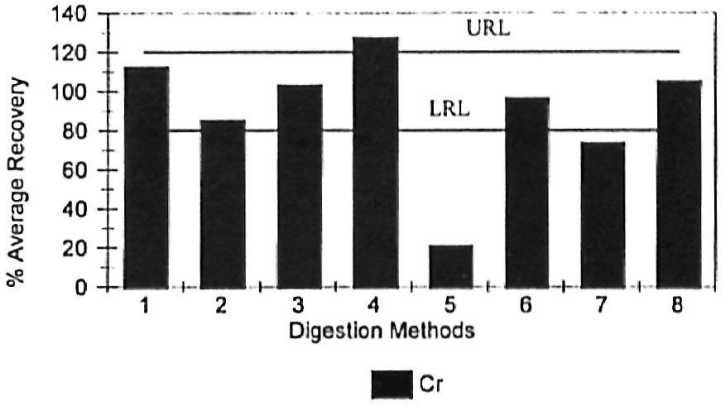

Fig 2: Recovery percentages of Chromium with different acid digestion solutions

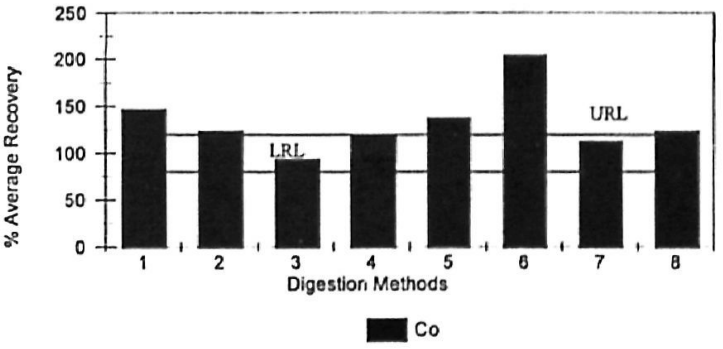

Fig 3: Recovery percentages of cobalt with different acid digestion solutions

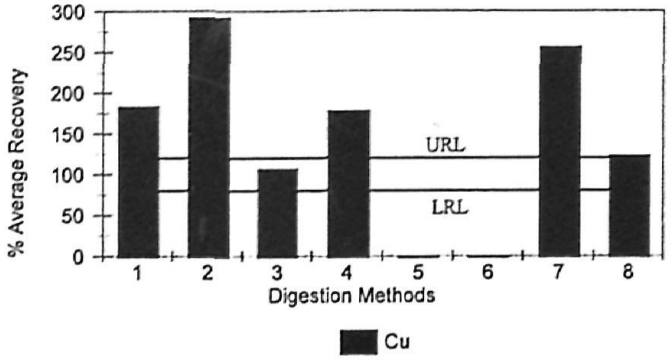

Fig 4: Recovery percentages of copper with different acid digestion solutions

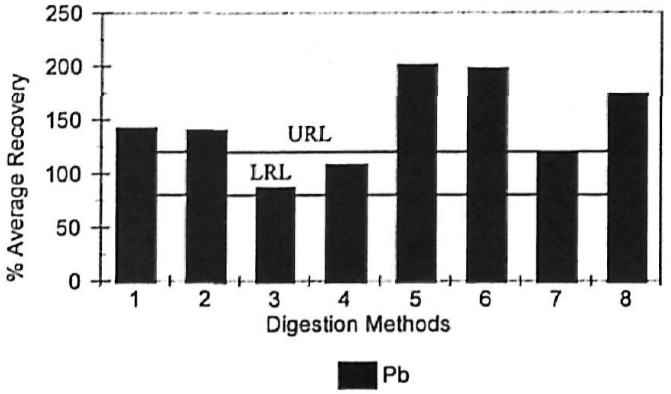

Fig 5: Recovery percentages of lead with different acid digestion solutions

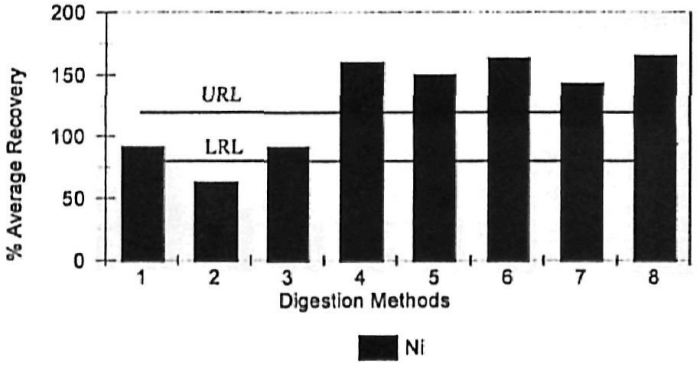

Fig 6: Recovery percentages of Nickel with different acid digestion solutions

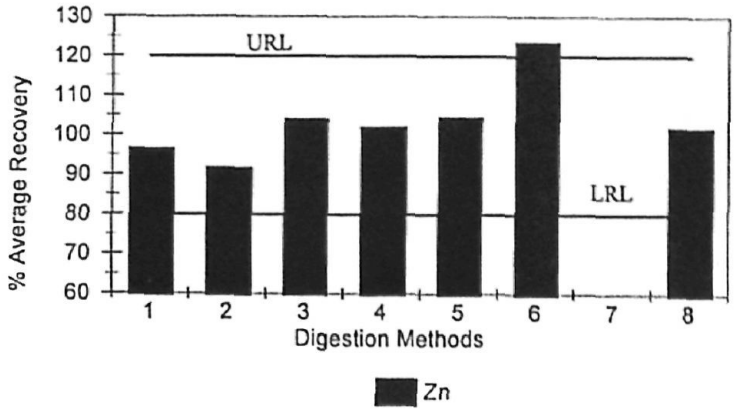

Fig 7: Recovery percentages of zinc with different acid digestion solutions

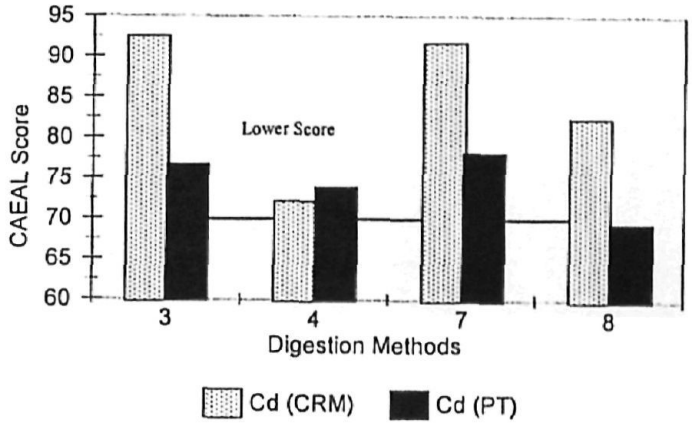

Fig 8: Validating the selected methods for determination of Cadmium in soil and sediment using PT samples of June, 2007 round and CRM 2703

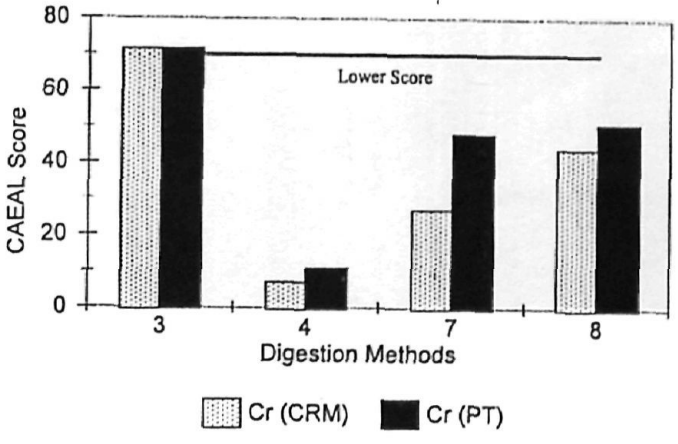

Fig 9: Validating the selected methods for determination of Chromium in soil and sediment using PT samples of June, 2007 round and CRM 2703

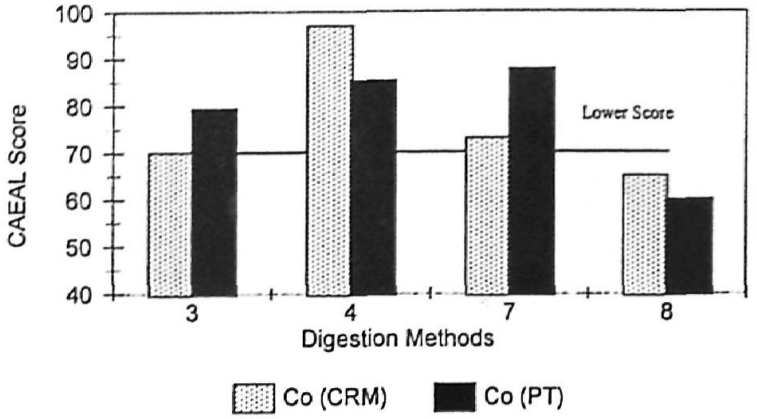

Fig 10: Validating the selected methods for determination of Cobalt in soil and sediment using PT samples of June, 2007 round and CRM 2703

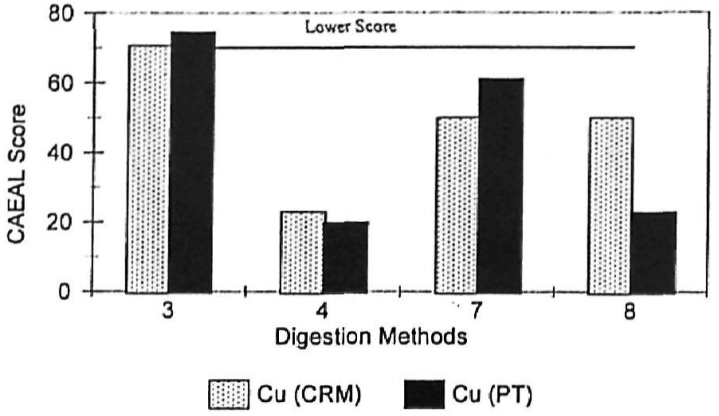

Fig 11: Validating the selected methods for determination of Copper in soil and sediment using PT samples of June, 2007 round and CRM 2703

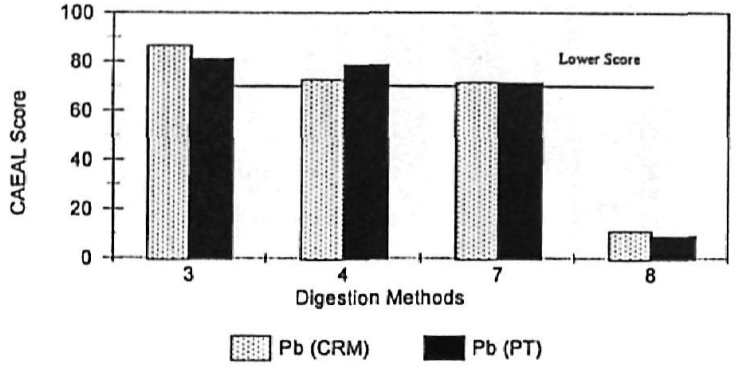

Fig 12: Validating the selected methods for determination of Lead in soil and sediment using PT samples of June, 2007 round and CRM 2703

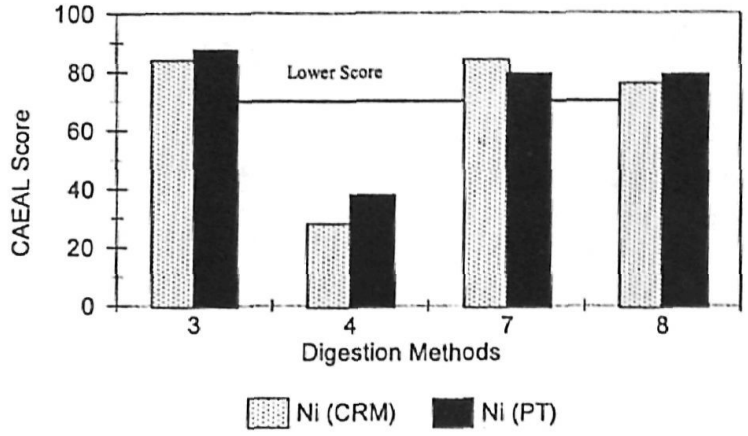

Fig 13: Validating the selected methods for determination of Nickel in soil and sediment using PT samples of June, 2007 round and CRM 2703

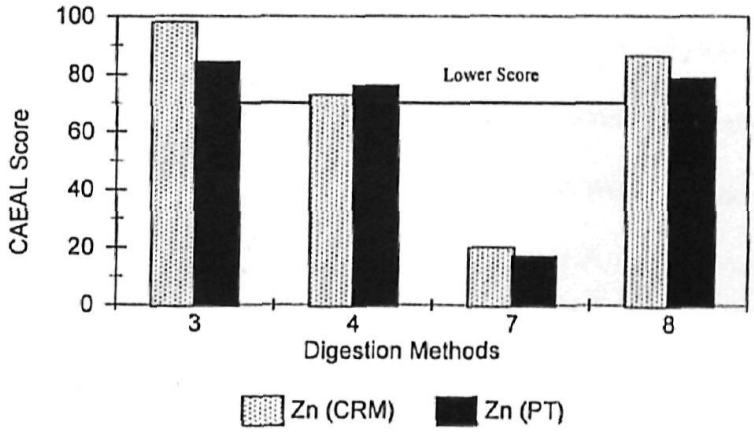

Fig 14: Validating the selected methods for determination of Zinc in soil and sediment using PT samples of June, 2007 round and CRM 2703