Research Article

Comparison of three methods for measuring heavy metals in calcareous soils of Iran

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Abstract

The exact estimation of the heavy metals concentration in different soils is very important for determining the degree of soil contamination. This study was designed to determine the ability to extract heavy metals (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, V and Zn) in calcareous soils using standard methods of digestion (ISO 14869-1, ISO 11466 and EPA 3050B) and the effect of lime on their extraction. In this study, 15 different soils with a wide range of chemical and physical properties and heavy metal concentrations and two reference materials were used. The results showed the percentage recovery in the reference material analyzed for the ISO 14869-1 method is between 94 and 107.8%, for the ISO 11466 method is between 90.3 and 101.7% and for the EPA 3050B method varied between 84.6 and 105.9%. The results showed that the recovery rate in the ISO 14869-1 method is better than the other methods (5% average for all elements). The results of natural soils were compared with total digestion method ISO 14869-1, and the efficiency of Cd extraction by ISO 11466 was between 61.25 and 97.12%. The extraction efficiency for As varied between 60.39 and 96.64%. The extraction efficiency for the Co, Cr, Cu, Mn, Ni, Pb, V and Zn elements was, respectively, between 71.2–96, 64.53–97.8, 66.07–96.3, 76.54–99.25, 79.3–100, 79.3–97.69, 73.43–95.30, and 73.7–99.9%. The extraction efficiency of Cd by the EPA 3050B method was between 60.25 and 96.34%. The extraction efficiency for As varied between 37.61 and 97.72%. The extraction efficiency for the Co, Cr, Cu, Mn, Ni, Pb, V and Zn elements varied between 46.32–72.46, 47.61–71.66, 44.84–86.55, 49.21–76.64, 76.95–96.73, 43.38–99.9, 43.17–81.12, and 45.83–72.69%, respectively. Based on the results, the ISO 11466 (Aqua regia) method is suggested as a suitable method for environmental studies in calcareous soils. The results showed that lime percentage has no effect on the recovery of the elements in calcareous soils.

Keywords Heavy metals · Calcareous soils · Extraction efficiency · ISO 11466 · EPA 3050B

1 Introduction

Heavy metals are considered as the main inorganic contaminants in the environment due to their negative impact on living organisms and their disordering of the environmental balance [3]. Heavy metals occur naturally in the environment with differences in their concentrations. However, the ecosystem has been influenced and polluted by heavy metals generated from anthropogenic sources such as the disposal of residues from fossil fuel combustion processes and from different branches of the metallurgical, mining, and chemical industries [2]. High levels of heavy metals in sediment and soil may enter the water, groundwater and plants, and enter the body of human and animals from the cycle. Therefore, the use of simple and precise methods for investigating heavy metals in environmental studies is important. Now, an accurate estimate of the concentration of heavy metals in soil and various ecosystems is a major challenge. So, varied digestion methods are used including: use of concentrated acids such as

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hydrofluoric acid (HF), hydrochloric acid (HCl), nitric acid (HNO_3), perchloric acid ($HClO_4$) and sulfuric acid (H_2SO_4). Different devices are used for digestion, such as beakers that are placed on a hot plate, digestion tubes in the digestion blocks and digestion vessels in microwave ovens [17]. Digestion methods, including conventional digestion and acid digestion by microwave, are widely used to prepare samples for spectroscopic analysis. Conventional methods are the use of open vessels that are extracted from the heat in the mixture of acids. The conventional methods have many advantages, such as relatively cheap and low cost devices, and reduce the need for advanced treatment of samples. However, the conventional digestion methods have a long time and different stages for analysis, and they are labor intensive, arduous and tedious and often contain high contamination potential [43]. High-sensitivity spectroscopy techniques such as flame atomic absorption spectroscopy (FAAS) and graphite furnace atomic absorption spectroscopy (GFAAS), inductively coupled plasma emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) have been broadly applied to measure the concentration of heavy metals in environmental samples [43]. These techniques have a disadvantage that they first require the solid sample to be transformed into solution where the metal content is determined (Prichard et al. 1996). Among the reagents, HCl, HNO_3 and HF are the most widely used reagents to digest the calcareous soils [42]; H_2O_2 is used in some cases [10]. These reagents are generally used in environmental studies. HCl and HNO_3 solubilize carbonates and phosphates, H_2O_2 and HNO_3 oxidize organic matter, and HF degrades the structure of aluminosilicates. Most studies emphasize that having complete digestion, the use of HF is necessary to break silicates [35]. Soil treatments with HF and $HClO_4$ provide satisfactory results for the decomposition of both organic and mineral sections in the soil. The hydrofluoric acid, through the reaction of F with Si, and the formation of SiF_4, with strong acid when it is heated, is a volatile compound and decomposes silicates. $HClO_4$ is also useful to eliminate the excess HF in the sample. However, long-term use of HF is dangerous and not recommended for routine and common analyses [52].

In studies, recovery for calcareous certified reference material when used with HF has been reported very low (less than 45%) to very high (more than 173%) depending on the element [1, 42]. Therefore, using HF may be suitable for some elements and not acceptable for some other elements. Method 3050B is considered as a conventional method because this method is performed in the open system and the elements are extracted with nitric acid and hydrochloric acid using a thermal source. This method has a disadvantage in this way that the atmospheric pollution risk and waste of elements are most volatile, such as

mercury [4]. Moreover, it should be noted that the 3050B method is not a complete digestion because its recovery is not 100% [44]. Simplicity and adaptability as a common and routine procedure have resulted in the wide use of the aqua regia method to determine amount of Cd, Cr, Cu, Ni, Pb and Zn elements in contaminated soils and sediments [17, 31]. The Aqua regia method or ISO 11466 is used to extract the recoverable amounts of heavy metals in soils and provides an estimation of the maximum availability of these metals for the plant. The remaining metals that are not released with Aqua regia are the bound part to the silica mineral fraction, and it is assumed that the estimation of the mobility and behavior of that element is not important [37]. Nitric acid reacts with concentrated hydrochloric acid and produces Aqua regia: $3HCl + HNO_3 \gg\gg 2 H_2O + NOCl + Cl_2$. However, in carbonate-rich materials, a significant amount of HCl is used to neutralize lime. Under such circumstances, the correct formation of Aqua regia is doubtful (ISO 11466 [19]). This method is used to adjust the estimation of the effect of soil amendments such as sewage sludge on the environment in many countries [25, 30]. Currently, many methods are used to quantify the amount of heavy metals in the soil, which requires examining the sample in a solvent form [48]. However, there is no international agreement on the unique digestion method that enables us to interpret the results in the same form in different parts of the world [38]. On the other hand, it is important to know how many elements in the soil are extracted by ISO 11466 and EPA 3050B methods compared to the total digestion method [38]. Studies show that there is a difference between digestibility and inappropriate yield in calcareous soils [29]. The accuracy of different digestion methods is variable in determining the concentration of total heavy metals in terms of the type of metal and soil properties [11]; therefore, first, a wide range of chemical and physical properties and the chemical of contaminated soils must be selected and different methods of digestion applied to determine the concentration of total heavy metals after determining the type of contamination. The total concentration of these metals indicates the dispersion and contamination level compared to the world standard level. The main objectives of this research include: (1) comparing three standard methods of ISO 14869-1, ISO 11466 and EPA 3050B in order to determine the concentration of 10 heavy elements (arsenic, cadmium, cobalt, chromium, copper, manganese, nickel, lead, vanadium and zinc) using two certified reference materials and 15 natural soil samples, (2) measuring the effect of soil properties, particularly lime, on the recovery percentage of heavy metals and (3) recommending the most proper and practical method depending on the type of element, digestibility and objective to measure the given elements.

2 Materials and methods

2.1 Area of study

Soils with different physical and chemical properties and different land use and heavy metal contaminants were selected. Soil samples were collected from the of East Azerbaijan, Kurdistan, Zanjan, Arak, Qom, Alborz, Semnan and Khorasan Razavi provinces (Fig. 1). The focus was on the areas with the possibility of contamination.

2.2 Collecting and preparing the soil

Fifteen soil samples were collected from depths of 0–15 cm from different provinces. The soil samples were dried at room temperature and passed through a sieve of 2 mm. Soil texture tested by hydrometer method [9], pHs, ECe in soil saturation extract [14] soil organic matter by oxidation method with potassium dichromate [57] and lime by calcimeter method [27].

2.3 Reagents

Suprapure acids were provided by Merck company: HCl (37% W/V), HNO₃ (65% W/V), HF (40% W/V) and HClO₄ (70% W/V) (Suprapure, Merck). The lime (CaCO₃) used was also purchased from Merck Company. The calibration of the equipment's was performed with standard tetrazole (Merck) solutions containing 1 g l⁻¹ from the element for device analysis. High-purity water (electrical conductivity < 10 MΩ) was used. All glass containers used were placed in 10% nitric acid overnight and then washed with distilled water.

2.4 Digestion methods

2.4.1 ISO 14869-1

Samples of 0.5 g were carefully weighed in polytetrafluoroethylene containers, and 5 ml of concentrated HNO₃ was added. The container was placed on a hot plate at 150 °C and heated it until the volume of the solution reached about 1 ml and then cooled to room temperature. This step repeated more than twice to ensure complete oxidation of soil organic
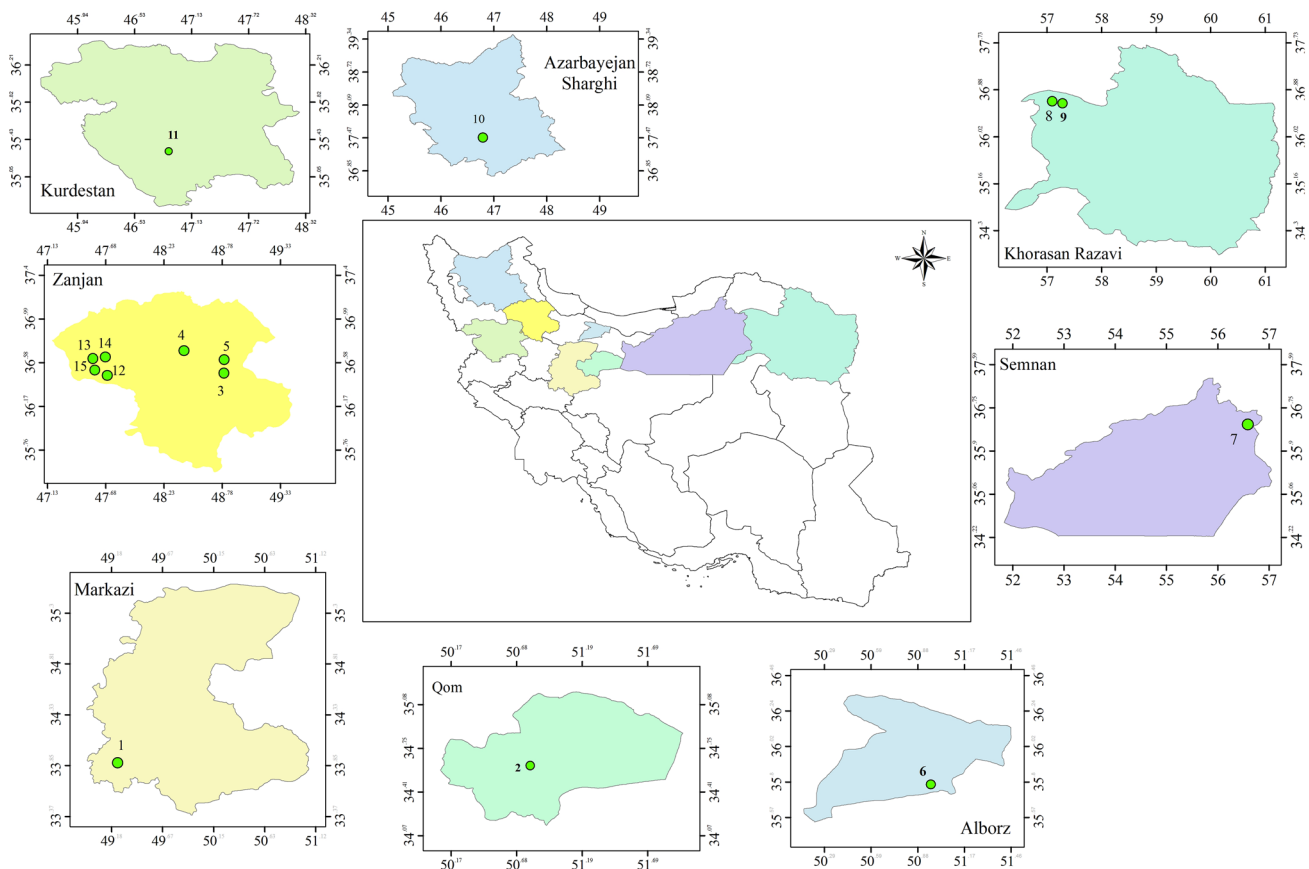

Fig. 1 Map of sampling points from the different province of Iran

matter. After cooling, 5 ml of HF and 1.5 ml of $HClO_4$ were added. The mixture was placed on a hot plate and heated up until the vapor perchloric acid and silicon tetrafluoride (SiF_4) were stopped. This step was repeated more than once. After cooling, 5 ml of distilled water and 2 ml of concentrated HCl were added and heated at low temperature to dissolve the remaining sediment. After cooling to room temperature, the sample was filtered in a 50-ml volumetric flask and distilled water was added up to 50 ml and stored in 4 °C temperature for further analysis (ISO 14869-1 2001) [20].

2.4.2 ISO 11466

Soil samples of 3 g were carefully weighed and transferred to the digestion tubes. At first, the pretreatment step was carried out at room temperature for 16 h with 28 ml of mixture (1:3) of 12 molar HCl and 17 molar HNO_3 to slowly oxidize soil organic matter. Then, the mixture was connected to the reflux system and increased the heat to maintain reflux flow and continued reflux for 2 h. After cooling to room temperature, the mixture was filtered to 100 ml volumetric balloon with a filter paper without ash Whatman 41 and washed with 0.5 M nitric acid and stored in polyethylene bottles at 4 °C for analyses (ISO 11466 1995) [19].

2.4.3 EPA 3050B

A method recommended by Environmental Protection Agency (EPA 3050B) was used as the conventional acid digestion method. Briefly, 1 g of soil samples was placed in a 250-ml flask for digestion. In the first step, 10 ml of HNO_3 (1 : 1) was added to the sample and mixed then covered with watch glass in the digestion flask. The sample was refluxed without boiling for 10 to 15 min at 95 ± 5 °C. After cooling, 5 ml of concentrated HNO_3 was added and refluxed for 30 min. this process was continued until the other brown vapors were removed from the sample. Using a watch glass, the sample was heated at boiling point of 95 ± 5° C and the solution was allowed to evaporate and the solution volume was reduced to about 5 ml. After cooling, slowly and without waste, 10 ml of 30% H_2O_2 was added and heated. Then, the sample was heated with 10 ml 37% HCl at 95° C for 15 min. The extract obtained was filtered through a 0.45-μm membrane paper, diluted to 100 ml with deionized water and stored at 4 °C for analyses. The total extraction process lasted for 180–200 min (USEPA 3050B) [55].

2.5 Assessing the effect of lime percent on heavy metal recovery in Aqua regia media (ISO 11466)

In order to assess the effect of lime on the formation of the Aqua regia media and the decrease in recovery of elements in the presence of lime, certain amount of lime (Merck) was added to the reference material of METRA-NAL™ 34 so that the concentrations of 10, 20, 30, 40 and 50% lime were obtained. Then, the amount of heavy metals measured by ISO 11466.3 method and the percentage recovery of the elements were calculated.

2.6 Heavy metal analysis

Concentrations of As, Co, Cr, Cu, Mn, Ni, Pb, V and Zn in final solutions digested with ICP Perkin Elmer Optima 2100 DV (USA) and Cd concentration with GFAAS Perkin Elmer 900Z (USA) were measured. The operating conditions of the ICP and GFAAS devices are presented in Tables 1 and 2. The instruments were calibrated daily with standardized solutions. The analysis of the sample was performed only if the R^2 calibration curve was greater than 0.99. A calibration check solution was prepared by another certified solution, and the calibration curves were checked after the initial calibration for every 10 samples. In the case of more than ± 10% deviation, the instruments were re-calibrated. To calculate the limit of detection the equipment, the concentration of heavy metals in the control solution of 2% nitric acid was read ten times. The limit of detection was calculated using 3σ, and the limit of quantitation by 10σ [29]. The wavelength used for each element, R^2, calibration curve slope (m), limit of detection and limit of quantitation for the instrument are presented in Table 3.

2.7 Quality assurance and quality control

Two certified reference materials (CRMs) including METRANAL™ 33 and METRANAL™ 34 purchased from Chinese METRANAL™ Company were digested in two

Table 1 Instrumental operating parameters for ICP-OES Perkin Elmer Optima 2100 DV

Parameter (unit)	Value
RF power (w)	1350
Plasma flow (l min^{-1})	15
Auxiliary flow (l min^{-1})	0.8
Nebulizer model	Cross-flow
Nebulizer flow (l min^{-1})	0.8
Sample flow (ml min^{-1})	2
Gases	Argon and nitrogen
Share gas	Air
Plasma viewing	Axial
Read delay per replicate (s)	45
Number of replicates	2
Measurement processing mode	Area
Calibration type	Zero intercept, linear

Table 2 Instrumental operating parameters for GFAAS Perkin Elmer 900Z

Parameter (unit)	Cd
Argon flow (ml/min)	250
Sample volume (µl)	20
Slit width (nm)	0.7
Heating program temperature, °C (ramp time (s), hold time (s))	
Drying 1	110 (1,30)
Drying 2	130 (15,30)
Ashing	500 (10,20)
Atomization	1500 (0,5)
Cleaning	2450 (1,3)

replications using three methods and analyzed for QA/QC calculation. Table 6 shows the recovery of heavy metals in two certified reference materials, which are digested by three methods. For each digestion method, two blank samples were taken and their amount was adjusted. To calculate the methods' limit of detection for digesting heavy metals' concentration in the blank sample, 10 times its reading and standard deviation (σ) were calculated and the limit of detection was calculated using 3σ and the limit of quantitation using 10σ [29] (Table 5). Recovery percentage was calculated from the following equation.

$$Recovery\ (\%) = \frac{\text{Measured value}\left(\frac{mg}{kg}\right)}{\text{Certified value}\left(\frac{mg}{kg}\right)} \times 100$$

Extraction efficiency (EE), expressed in percentage, was obtained from the ratio of extracted element amounts using the partial digestion methods of EPA3050B and ISO 11466 to the total digestion method of ISO 14869-1 [38].

2.8 Statistical analysis

SAS 9.2 software (SAS [18] was used to calculate mean, standard deviation and Pearson correlation coefficient (r). Also, SigmaPlot 14.0 software was used to draw charts.

3 Results and discussion

3.1 Physical and geochemical characteristics of soils

Soil No. 1 is from Arak, which is sampled around the Lakan lead and zink mine. The geological formations of the region include Cretaceous sediments, alluvial fans, anhydrite, argillaceous limes, and major minerals include sphalerite (ZnS), gallon (PbS), anglesite ($PbSO_4$) and cerussite ($PbCO_3$) [58]. Soil No. 2 was sampled from the pasturages of Qom. Soil Nos. 3, 4 and 5 were sampled from arable, forest and pasturages in Zanjan, which included alluvial terraces and quaternary alluvial deposits [40]. Sample No. 6 obtained from soil and water research farm was artificially contaminated with cadmium and lead and was remained for four years in normal conditions to achieve a state of condition. Soil No. 7 was from Semnan, and 8th and 9th soils were collected from the chromite Feroomad mine in Khorasan Razavi. The units of rock in this area are made from ophiolitic units (Hazburiti, Serpentine, Gabbro and Donit) as well as volcanic and pyroclastic units with Neogene age and limestone of Cretaceous age. Chromites in the region are pedopharm chromite. Also acidic stones with structure of conglomerate, sandstone, tuff, tofite and acid agglomerates were found in this area. Chromite ($FeCr_2O_4$), crocusite ($PbCrO_4$), millerite (NiS), nickelite (NiAs) and brittle polyethylene (NiSb) are major regional

Table 3 Instrumental detection limits and Limit of Quantitation ($\mu g\ l^{-1}$) for ICP Perkin Elmer Optima 2100 DV and GFAAS Perkin Elmer 900Z

Element	Wave Length (nm)	R^2	Claib. Range used (mg l^{-1})	Slope	LOD	LOQ
As	193.696	0.9997	2	0.31	10	33
Cd*	228.80	0.996	0.005	0.059	0.2	0.7
Co	228.616	0.9997	2	13.04	0.85	2.80
Cr	267.716	0.9998	5	44.03	1.25	4.13
Cu	327.393	0.9999	2	71.25	0.97	3.2
Mn	257.610	0.9998	20	149	1.4	4.6
Ni	231.604	0.9998	2	11.52	1.32	4.37
Pb	220.353	0.9994	2	1.34	3.2	10.56
V	292.464	0.9998	5	3.53	3.6	11.88
Zn	206.200	0.9996	2	3.61	7	23.1

The cadmium concentration was read by GFAAS and other elements with the ICP instrument

minerals [6]. Soil Nos. 10 and 11 were sampled east Azarbaijan and Kurdistan province; soil origin of the area is made of sedimentary and volcanic deposits that contain yukonite [$Ca_7Fe_{12}^{3+} (AsO_4)10(OH)_{20}15H_2O$], arsenopyrite (FeAsS), orpiment (As_2S_3) and realgar (As_4S_4) [8], [24]. Soils Nos. 12–15 were sampled around the Anguran mine in Zanjan, located on Shist Anguran Formation. Anguran kansar consists of two parts. An initial sulfide fraction is composed primarily of sphalerite (ZnS), gallon (PbS) and pyrite (FeS_2), and a secondary carbonate element derived from the sulfide alteration and the development of its sub-stitution phenomenon is mainly composed of anglesite ($PbSO_4$), Cerussite ($PbCO_3$) and smithsonite ($ZnCO_3$) [32].

The range of clay content in soil samples was between 6 and 41%, the lowest amount was related to Anguran lead and zinc mine in Zanjan, and the highest amount of clay related to pasturage in Zanjan. The variation of organic matter changes ranged from 0.03% to 2.87%, the lowest amount was related to the sample of Qom, and the highest amount was in the pasturage area of Zanjan. The range of lime changes was between 2.21 and 61.2%, with the highest amount of lime from sample 3 from arable region in Zanjan, which includes alluvial carbonate terraces and argillic limes. The pH value was from 6.3 to 8.2, with high pH in most soils indicating limestone and alkalinity of the soil. The EC value was different from 0.39 to 46.3 dS/m (Table 4).

3.2 Limit of detection and limit of quantification of methods

The limit of detection and limit of quantitation for different digestion methods are presented in Table 5. The limit of detection (LOD) ranged from 0.8 to 12.79 µg l^{-1}, and the limit of quantitation (LOQ) varied from 2.64 to 42.22 µg l^{-1}. Both the limits of detection and quantification are comparable with that obtained by Sandroni and Smith [41] and Marin et al. [29]. Chemical Blank unlike analytical blank, the digestion processes are completely done and therefore the LOD and LOQ are higher in them. The amount of LOD and LOQ in the comparison of digestion methods for the elements (Cd, Co, Cr, Co, Pb, Zn, Mn and Fe) varied between 0.5–30 and 2–99 µg l^{-1}, respectively. [29].

3.3 Recovery of digestion methods

The recovery percentage of different digestion methods is presented in Table 6 for two reference materials, METRA-NAL™ 33 and METRANAL™ 34. The results of three methods of digestion with a certified amount in the reference material were acceptable in the most elements. The recovery range varied between 84.6 and 107.8%. The recovery percentage in the ISO 14869-1 method, which uses HF and

Table 4 Some of physical and chemical properties soil selected

Soil number	City	Land use	Specific information	Clay (%)	Silt (%)	Sand (%)	Texture	OC (%)	pH	EC (dS/m)
1	Arak	Surrounding Lakan zinc and lead mine	Cretaceous sediments, alluvial fans	34	47	34	Silty clay loam	0.86	7.5	0.84
2	Qom	Pasturage	–	6.6	4.2	89.2	Sand	0.03	7.86	0.79
3	Zanjan	Arable	Alluvial terraces and quaternary alluvial deposits	35.7	33.5	30.8	Clay loam	0.5	7.87	0.41
4	Zanjan	Forest		12.8	27.8	59.4	Sandy loam	1.18	7.86	7.4
5	Zanjan	Pasturage		41.04	36.95	22.01	Clay	2.87	7.84	2.1
6	Alborz	Arable	–	18	47	35	Loam	0.61	8.2	0.67
7	Semnan	Surrounding Chromite Freud mine	Ophiolitic units, pyroclastic units	14						
8	Khorasan Razavi	Surrounding Chromite Freud mine		11	12	77	Sandy loam	1.04	7.93	1.03
9	Khorasan Razavi	Surrounding Chromite Freud mine		18	27	55	Sandy loam	0.43	7.96	2.84
10	East Azarbaijan	Arable	Sedimentary and volcanic deposits	11.92	9	79.08	Sandy loam	0.32	7.4	0.42
11	Kurdistan	Arable		15.56	24.72	59.72	Sandy loam	0.56	7.8	0.39
12	Zanjan	Surrounding zinc and lead Anguran mine	Shist Anguran Formation	26.64	34	39.36	Clay loam	1.08	7.5	0.8
13	Zanjan	Surrounding zinc and lead Anguran mine	Shist Anguran formation	30	24.66	45.34	Sandy clay loam	0.98	7.7	0.59
14	Zanjan	Surrounding zinc and lead Anguran mine	Shist Anguran formation	26.32	23	50.68	Sandy clay loam	0.74	7.9	1.32
15	Zanjan	Surrounding zinc and lead Anguran mine	Shist Anguran Formation	6	23	71	Sandy loam	0.11	6.3	46.3

Table 5 Limit of detection and limit of quantitation ($\mu g\ l^{-1}$) for digestion methods

Element	Method					
	ISO 14869-1		ISO 11466		EPA 3050b	
	LOD	LOQ	LOD	LOQ	LOD	LOQ
As	10.25	33.83	12.79	42.22	10.21	33.7
Cd*	0.03	0.1	0.04	0.12	0.02	0.06
Co	0.89	2.93	0.9	3	0.98	3.24
Cr	1.26	4.16	1.7	5.6	1.44	4.76
Cu	1.29	4.27	1.08	3.55	1.2	3.95
Mn	3	9.9	10	33	3.72	12.26
Ni	1.42	4.69	1.51	4.97	1.79	5.92
Pb	4.9	16.17	7.11	21.33	5.12	16.7
V	3.62	11.94	4.1	13.45	6.48	21.38
Zn	8.74	28.85	7.66	25.3	7.63	25.17

* The cadmium concentration was read by GFAAS and other elements with the ICP instrument

$HClO_4$ in the digestion process, was different between 94 and 107.8%. The recovery percentage of this method was less than the certified value for all elements measured in the standard error range of the reference substance, with the exception of Mn in the reference material METRANAL™ 34. Also, this method had overestimate in As, Cd, Co and Cu. Adamo et al. [1] reported a recovery percentage in reference material CRM 141R when using HF for Cd and Co 115 and 147%, respectively. The recovery percentage in calcareous material was reported when using HF for 118, 118, 126 and 129% digestion for Cd, Cr, Cu and Ni elements [42]. The recovery percentage in the NIST SRM 2704 reference material was different between 86 and 113% when it was digested with HNO_3–$HClO_4$–HF for Cr, Cu, Ni, Mn, Pb and Zn [50].

The recovery percentage in the ISO 11466 method was different between 90.3 and 101.7%. All measured elements by this method have acceptable recovery percentages and were approved within the standard error range of the reference material, except for the Cu that was underestimated in the reference material METRANAL™ 33 and underestimated in the reference material METRANAL™ 34 for Cu and Co. Cd was overestimated in both reference materials. The recovery percentage of Cu, Ni and Pb in reference substance IAEA-405 was 110, 105 and 114%, respectively, with standard spikes to reference material [38]. The recovery percentage in reference material CRM 141R was reported to be 98, 98, 84, 94, 89, 82 and 101%, respectively, according to ISO 11466 for Cd, Co, Cr, Cu, Mn, Pb and Zn elements [29]. The recovery percentage of elements in the reference material LGC6187 was reported to be 110, 104, 103, 89 and 105%, respectively, according to ISO 11466 for Cr, Ni, Co, Zn and As [13]. The recovery percentage of elements was 96, 103, 95, 84 and 96%, respectively, according to ISO 11466 for reference material CRM

142 for Cd, Co, Ni, Pb and Zn elements and was reported to be 98, 101, 98, 96 and 102%, respectively, for reference material CRM 143 [35].

The recovery percentage of the elements in the EPA 3050B method was different between 84.6 and 105.9%. The measurement of As, Pb and Zn was underestimated in the reference material of METRANAL™ 33, and there was overestimate in Cd and Cu. There was underestimate in the reference material METRANAL™ 34 in As measurement, and there was also overestimate in the Cu element. The recovery percentage in San Joaquin Soil-2709 Reference Material for Cr, Cu, Pb and Zn was reported to be 87.6, 62.1, 36 and 79.7%, respectively, according to 3050B and was 85.1, 61.9, 38.5 and 85.5% for the reference material Estuarine Sediment-1646A, respectively [15]. The recovery percentage for the reference material NIST 2710 was 3050B for the elements Cu, Pb, Zn, Cr and Ni, respectively, and was 99, 103, 90, 59 and 49 was 97, 107, 97, 49 and 78%, respectively, for the NIST 2711 [26].

3.4 Assessing the effect of lime on heavy metal recovery in ISO 11466

Figure 2 shows how different lime percentages affect the recovery of heavy metals in reference material METRANAL™ 34. Lime with the consumption and neutralization of some HCl in the formation of the Aqua regia media causes the reduction in the recovery of the elements (ISO 11466 1995). As it is clear, the amount of lime has no effect on the recovery of most elements. In the Cr element, it reduces the recovery percentage that is within the limit of the standard error, and likely this difference was caused by instrument error. In the Cu element, the lime has been estimated to be higher, but this amount was more than estimated level within the standard error range of the

Table 6 The percentage of recovery content heavy metals (mg kg^{-1}) (mean ± standard deviation) by different digestion methods in two certified reference materials

Element	Silty clay loam-METRANAL™ 33					METRANAL™ 34-Loam				
	Total certified	Aqua regia certified	ISO 14869-1	ISO 11466.3	EPA 3050B	Total certified	Aqua regia certified	ISO 14869-1	ISO 11466.3	EPA 3050B
As	16.7	11.6±0.7	17.28±0.08 (103)*	11.51±0.03 (99.2)	9.82±0.1 (84.6)	49.6±3	42.4±2.2	44.81±1.45 (90.3)	40.9±0.35 (96.5)	39.04±0.34 (92.1)
Cd	0.32±0.04	0.32±0.03	0.35±0.15 (107.8)	0.33±0.1 (101.7)	0.33±0.33 (103.1)	1.52±0.15	1.44±0.07	1.54±0.1 (102)	1.45±0.1 (100.7)	1.43±0.15 (99.3)
Co	11.5±0.7	10.3±0.5	11.92±0.32 (103.6)	9.73±0.1 (94.5)	9.92±0.2 (96.3)	20±1.3	17.5±0.9	19.74±0.1 (98.7)	16.54±0.23 (94.5)	16.78±0.17 (95.9)
Cr	79.8±6.7	42.4±3.6	79.83±3.2 (100)	40.85±0.25 (96.3)	40.39±0.24 (95.3)	82.2±6.3	46.3±3.8	76.23±0.5 (92.7)	41.83±0.5 (90.3)	42.09±0.8 (90.9)
Cu	29.1±0.8	25.4±0.9	30.75±0.35 (105.7)	23±0.25 (90.6)	26.69±0.2 (105.1)	183±5	167±1	185.15±3.15 (101.2)	161.30±1.75 (96.6)	176.90±3.3 (105.9)
Mn	600±37	529±19	570.25±5.35 (95)	509.25±3.75 (96.3)	519.10±0.9 (98.1)	869±34	741±36	820.45±5.85 (94.4)	726±35 (98)	710.15±11.35 (95.8)
Ni	31.3±1.5	28.8±1.2	31.82±0.38 (101.7)	27.86±1 (96.7)	28.65±0.2 (99.5)	33.3±1.1	30.4±1.2	34.80±0.7 (104.5)	28.41±0.5 (93.5)	29.35±0.29 (97.1)
Pb	33.5±2.4	25.2±1.1	32.91±0.26 (98.2)	24.52±0.1 (97.3)	22.84±0.51 (90.6)	93.4±3.4	83.1±2.3	90.34±2.8 (96.7)	80.93±1.1 (97.4)	81±1.69 (94.8)
V	76.2±6.4	52.9±2.7	77.51±5.9 (101.7)	52.45±2.55 (99.1)	50.39±0.24 (95.3)	126±7	95.1±4.9	121.7±3 (96.6)	90.15±0.95 (94.8)	92.13±0.22 (96.9)
Zn	81±7.6	69.4±1.8	76.16±0.7 (94)	64.1±2.25 (92.3)	66.80±0.44 (96.2)	227±7	198±6	215±9 (94.7)	191.58±1.68 (96.8)	190±1 (96)

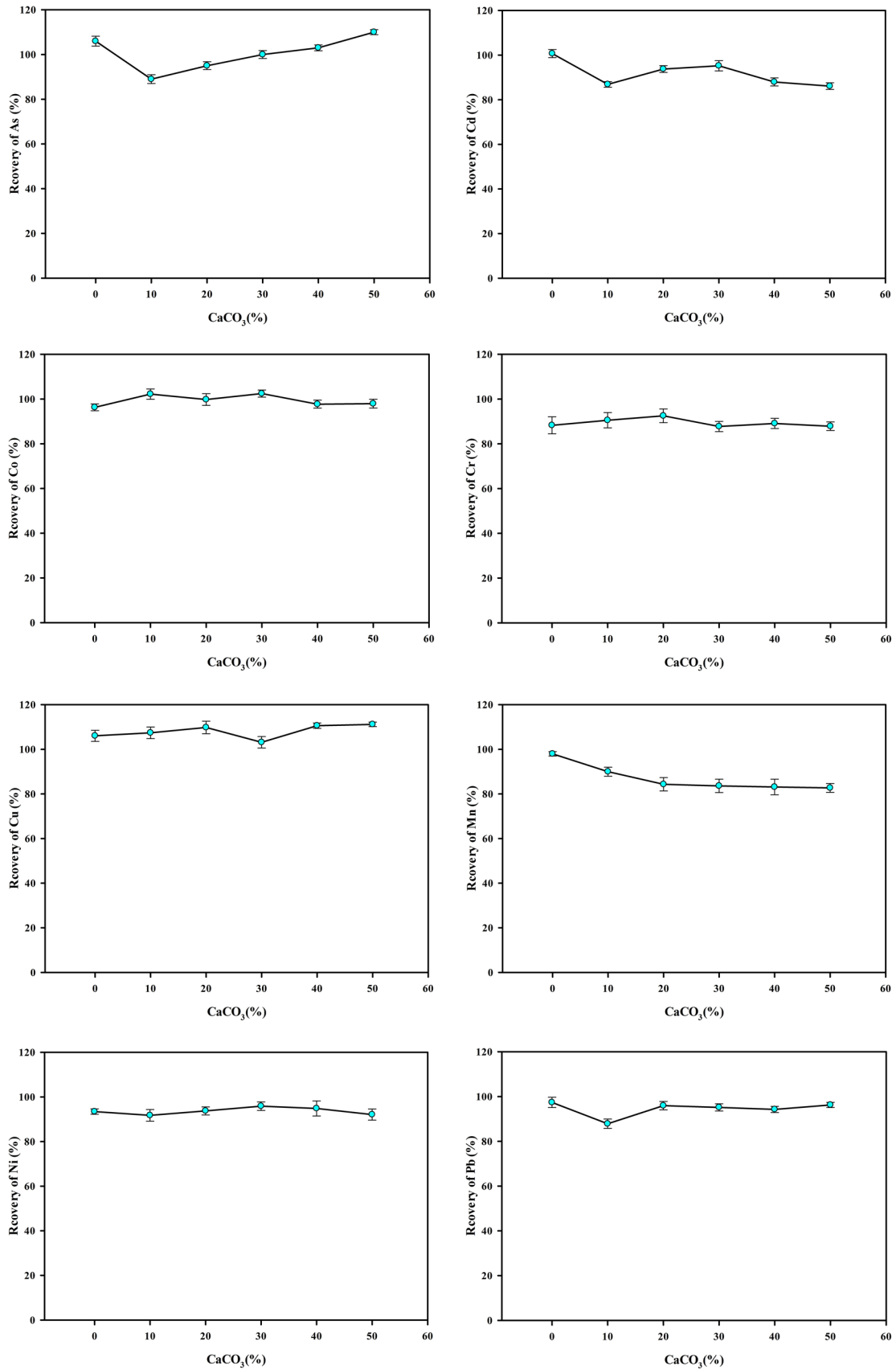*The numbers in parentheses are the percentage of recovery

Fig. 2 Percentage of recovery heavy metals (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn) in CRM METRANAL™ 34 At various concentrations of lime
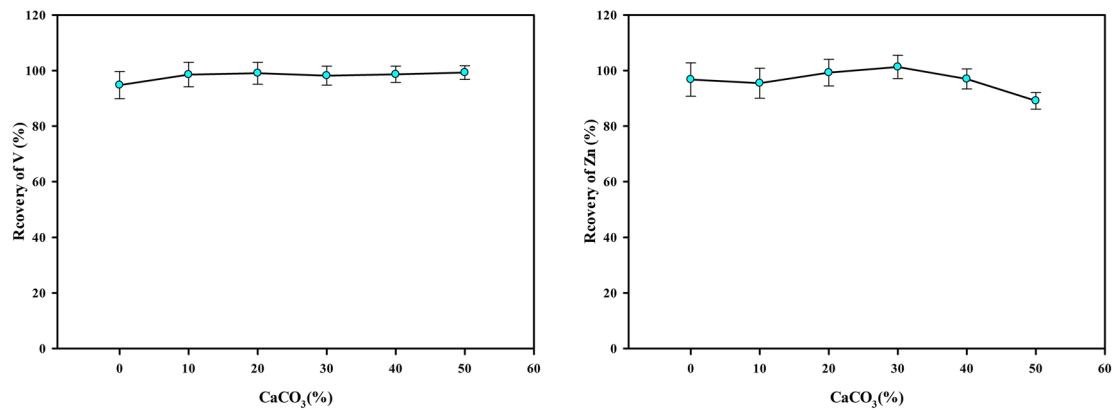
Fig. 2 (continued)

reference material. However, the Mn in quantities of more than 10% reduced the recovery rate and has no effect on recovery in the elements of As, Cd, Co, Ni, Pb, V and Zn.

3.5 Comparison of digestion methods in natural soil samples

Three methods of digestion were measured using 15 natural soils sampled from different regions of Iran with different physicochemical characteristics. We can examine the effects of different matrices and spectral interference in natural soil samples by these methods. Total digestion results according to ISO 14869-1 are shown in Table 7. As it is clear, using HF increases the ability to extract heavy metals from the soil. The total amount of As in soil samples was different between 4.09 and 1250 mg/kg. The amount of As in soil Nos. 11 and 15 was higher than the limit, which is related to Kurdistan and Zanjan. The origin of arsenic is geological and is made of arsenopyrite minerals (FeAsS), enargite (Cu_3AsS_4), orpiment (As_2S_3) and realgar (As_4S_4) in these areas. The total Cd content in soil samples is between 0.14 and 7.25 mg/kg. The amount of Cd was high in soil No. 6 which has been artificially contaminated. The total Co content in soil samples was between 6.26 and 320.15 mg/kg. Cr content of all soils was between 26.11 and 564.4 mg/kg, and the Cr content was higher in soil Nos. 7, 8 and 9, which are related to the Feroomad chromite mine. This chromium is originated from chromite ($FeCr_2O_4$) and crocoite ($PbCrO_4$) minerals. The amount of total Cu in all soils was between 33.98 and 184.35 mg/kg soil, and this high amount of Co in the soil No. 15 was related to enargite (Cu_3AsS_4) mineral. The total amount of Mn is different between 223.9 and 5598.5 mg/kg. Soil total Ni was different between 21.8 and 1131.1 mg/kg soil. The amount of Ni was high in soils 7, 8 and 9, which is likely related to millerite (NiS), niccolite (NiAs) and breithauptite (NiSb) minerals in the geological sediments of Feroomad mine area in Semnan. The total amount of Pb in all soils was different from 13.1 to 5742 mg/kg soil. The Pb content in soil sample one was high, which was related to the Lacan lead and zinc mine, that contains galena (PbS), anglesite ($PbSO_4$) and cerussite ($PbCO_3$) as the major regional minerals. High Pb content in sample 6 in Alborz is due to artificial contamination. The soil Nos. 12, 14 and 15 are related to the lead and zinc mine in Zanjan. The geological formations of the region consist of anglesite ($PbSO_4$) and cerussite ($PbCO_3$) minerals. The amount of vanadium of the soil was different from 35.26 to 328.45 mg/kg. The amount of total Zn in all soils varied between 43 and 8657.25 mg/kg. The amount of Zn was high in the soil 1, which was related to Markazi around the Lacan lead and zinc mine, which was originated from sphalerite (ZnS) mineral. Zn was high in soil Nos. 12, 14 and 15 sampled from Anguran lead and zinc mine in Zanjan, and the origin of zinc is from sphalerite (ZnS) and smithsonite ($ZnCO_3$) minerals. Using a mixture of acids increases the digestion efficiency [54]. The mixture of HCl, HNO_3, $HClO_4$ and HF acids dissolves most elements in the soils [51]. Using HF in soils results in the formation of Ca-F complex, which interferes with the analysis of the device. $HClO_4$ and H_3BO_3 should be used to prevent forming the complex [36]. Hydrofluoric acid affects greatly the digestion process because it breaks down the structure of the silicates and increases the results [35, 43]. However, using it can result in interference in a wide range of elements [1, 42]. Natural soil samples are more heterogeneous than reference materials, which can provide highly variable recovery values for metals due to different matrix effects [29].

Table 8 shows the results of heavy metals in 15 soil samples digested by ISO 11466. The efficiency of extraction of this method for As was different between 60.39 and 96.64%. The efficiency of Cd extraction was between 61.25 and 97.12%. The extraction efficiency was between 71.2–96, 64.53–97.8, 66.07–96.3, 76.54–99.25, 79.3–100,

Table 7 The concentration of heavy metals (mg kg^{-1}) in 15 soils analyzed by ISO 14869-1 (mean ±standard deviation) ($n = 2$)

Soil number	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Pb	V	Zn
1	54.92±2.57	8.71±0.69	26.83±2.49	100.84±5.56	68.43±2.61	3070.50±159.5	150.5±0.7	2218.5±62.5	2218.5±62.5	112.45±1.65	5013.5±19.5
2	4.09±0.14	0.22±0.05	29.15±2.33	65.32±2.81	56.32±2.14	1090.50±11.50	21.94±0.33	27.95±0.39	27.95±0.39	328.45±5.25	112.95±7.95
3	27.32±0.25	0.14±0.015	6.26±0.23	26.11±0.42	39.93±0.9	223.90±4.9	21.8±0.56	13.1±0.17	13.1±0.17	35.26±0.67	43±0.85
4	20±0.02	0.32±0.05	15.81±0.17	63.79±0.44	80.68±1.28	469.05±9.55	54.89±0.2	51.1±0.8	51.1±0.8	72.59±0.32	86.12±0.11
5	43.72±0.27	5.38±0.09	21.49±0.82	54.60±1.60	74±1.72	1284.5±47.5	48.80±0.8	59.80±2.64	59.80±2.64	103.75±1.45	261.95±5.75
6	26.87±2.14	13.36±0.1	17.51±0.45	46.88±3.27	43.33±1.2	844.2±44.1	32.82±0.44	289.2±4	289.2±4	101.6±1.2	82.45±0.11
7	30.5±1	0.2±0.05	30.35±2.69	290.5±1	85.11±5.63	1110.5±8.5	410±8.8	15.82±0.41	15.82±0.41	209.25±2.55	71.48±0.44
8	11.14±0.6	0.19±0.05	62.95±0.59	564.4±2	45.50±2.94	868.75±6.45	1131.1±5.45	18.66±0.17	18.66±0.17	78.69±1.06	66.30±1.94
9	18.28±0.25	0.91±0.03	27.40±0.58	150.1±9.5	85.96±3.7	808.3±26.7	187.5±2.3	18.25±0.02	18.25±0.02	123.05±5.55	77.05±1.82
10	26.08±0.45	0.17±0.17	17.13±0.7	39.97±0.36	36.19±1.89	433.85±9.65	38.08±1.05	16.06±0.47	16.06±0.47	95.80±1.42	60.61±0.94
11	1073.5±61	0.36±0.05	18.88±0.59	79.59±2.17	49.27±5.02	1216±20	65.28±0.75	25.73±1.2	25.73±1.2	74.81±0.55	87.14±0.62
12	64.30±4.71	3.49±0.1	20.57±3.36	54.82±0.54	38.60±0.6	810±24	55.49±0.48	181.20±2.7	181.20±2.7	66.93±0.51	435.3±2.7
13	38.71±0.48	1.37±0.016	18.59±1.33	66.44±1.19	36.39±3.28	689.15±3.5	76.74±0.38	69.72±0.4	69.72±0.4	67.85±1.14	137.45±4.85
14	100.72±2.19	2.78±0.03	13.36±0.36	38.67±0.94	33.98±0.45	638.5±3.5	32.88±0.1	241.25±4.35	241.25±4.35	54.73±0.64	140.05±2.25
15	1250±10	17.25±0.78	320.15±1.55	75.17±2.29	184.35±1.25	5598.50±35.5	205.4±5.6	5742±18	5742±18	70.04±0.87	8657.25±94.95

79.3–97.69, 73.43–95.3 and 73.7–99.9%, respectively, for the Co, Cr, Co, Mn, Ni, Pb, V and Zn elements. Poor extraction efficiency of the elements in samples 5, 3, 1, 13, 12 and 14 is likely related to high clay content. The low extraction percentage in soils Nos. of 4, 5, 12, 8, 13 and 1 is related to high organic matter in the soil. Niskavawara et al. 1997 reported that the rest of the elements in the soil solution not released by the Aqua Regia method are often bonded to silicate minerals. However, this group of heavy silicate compounds has no importance to estimate mobility and usability. Vercoutere et al. [56] reported an Aqua regia digestion method as an effective and useful method to determine the concentration of heavy metals. The Aqua regia method may be used to measure Cu, Ni and Zn in soils affected by human activities and therefore may be suitable to analyze regularly the heavy metal contamination in soils [16]. Manz et al. [28] used Aqua Regia to measure the content of Cu, Pb and Zn agriculture soils in Germany. Twyman [54] reported that Aqua Regia solution is effective in dissolving sulfides, phosphates and many metals and alloys such as Pt, Au and Pd. Determining the releasing part with Aqua Regia provides valuable information on the long-term presence of heavy metals in the soil. In this regard, the latest methods of digestion introduced by Aqua Regia have been used to dissolve various compounds [7]. Berrow and Stein [5] reported that Aqua regia extracts more than 70% of Cd, Mn and Ni from some sediment. Recovery ranging from 43% to 77% for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn was reported according to AGAL-11 reference sedimentation by Siaka et al. [46]. A study conducted by some researchers showed that extraction with Aqua regia resulted in the maximum recovery of acid-soluble elements [23] and resulted in recovery between 89% and 110% for some metals in soil and sediments [7]. Past work has shown that the use of Aqua regia for extraction may result in a low estimation of heavy metals amount such as Co, Cd, Cr and Ni up to 50% of the total amount [45, 53]. The reasons for this low estimation can be the type of matrix and the strength of the Aqua regia solution, which cannot dissolve silicates, iron oxides and aluminum oxides, metals of which can form with these bonding compounds. Studies have shown that the efficiency of the Aqua regia extraction solution is different in different soils. For example, this value for Cd has been reported between 43 and 90% in various studies, which is consistent with the values obtained in this study (61–97%). However, Sastre et al. [43] showed in their study that the difference between the total amount and the amount extracted with the Aqua regia solution cannot be considered as a general rule and may be highly affected by the studied element, the chemical composition of the matrix, organic matter and the solvent type used to extract all of the elements. Ni in the soil is with oxides and iron hydroxides that are not

Table 8 The concentration of heavy metals (mg kg^{-1}) in 15 soils analyzed by ISO 11466 (mean ± standard deviation) (n = 2)

Soil number	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	V	Zn
1	44.53±0.33 (81.09)*	7.53±0.1 (86.4)	25.32±0.67 (94.4)	96.40±1.03 (95.60)	65.9±2.23 (96.3)	2534±61.67 (82.53)	122.95±3.22 (81.7)	1759.2±8.83 (79.3)	89.88±1.28 (79.93)	3693.3±53.7 (73.7)
2	3.55±0.17 (86.72)	0.21±0.01 (100)	22.38±0.75 (76.8)	52.44±0.89 (80.29)	44.33±0.89 (78.7)	1058.92±9 (97.10)	21.33±0.11 (97.2)	26.4±0.88 (94.44)	294.58±0.75 (89.69)	96.93±3.53 (85.8)
3	20.61±0.42 (75.44)	0.13±0.01 (89.5)	4.49±0.25 (71.7)	19.94±0.5 (76.37)	29.54±0.29 (73.98)	214.58±7.83 (95.84)	20.15±0.5 (92.5)	10.4±0.41 (79.73)	32.32±1.15 (90.88)	33±0.72 (76.7)
4	13.28±0.8 (66.42)	0.27±0.02 (85.7)	11.44±0.24 (72.3)	51.40±0.54 (95.60)	64.45±0.7 (79.88)	644.21±7.13 (99.25)	53.82±0.32 (98.1)	46.3±0.76 (90.73)	53.3±0.71 (73.43)	85.54±0.62 (99.3)
5	28.52±0.25 (65.23)	5.15±0.01 (89.77)	16.10±0.17 (74.9)	35.23±0.21 (64.53)	58.63±1.24 (79.24)	1206.25±6.5 (93.9)	45.60±0.4 (93.5)	52.3±0.21 (87.5)	76.63±0.63 (73.86)	232.21±0.83 (88.6)
6	24.34±0.11 (90.6)	11.22±0.29 (83.98)	16.58±0.26 (94.7)	36.98±0.29 (78.89)	36.1±0.25 (83.27)	794±5.3 (94.1)	32.39±1.55 (98.7)	261.3±2 (90.34)	86.58±5.28 (85.22)	81.93±0.82 (99.4)
7	25.36±0.2 (83.16)	0.19±0.05 (95)	28.16±0.93 (92.8)	220.33±3 (75.85)	60.63±0.88 (71.25)	1065.8±23.5 (95.98)	392.50±1.67 (95.7)	15.5±0.91 (97.69)	194.72±7.12 (93.06)	61.28±2.68 (85.7)
8	9.15±1.59 (82.15)	0.14±0.02 (77.12)	61.80±1.37 (98.2)	552±2 (97.8)	34.2±0.8 (75.17)	2534±61.67 (82.53)	1001.17±2.83 (88.5)	17.8±0.67 (95.19)	72.67±2.17 (92.35)	60.30±2.53 (91)
9	15.63±0.33 (69.32)	0.81±0.02 (89)	24.29±0.69 (88.7)	130.87±2.62 (87.19)	78.74±1.96 (91.84)	806.5±2.33 (99.78)	176.92±4.08 (94.4)	15.5±1.27 (84.83)	107.57±1.55 (87.42)	73.43±2.58 (95.3)
10	18.08±1.14 (69.32)	0.16±0.01 (91.2)	15.83±0.1 (92.4)	34.24±0.65 (85.66)	26.38±0.41 (72.91)	376.96±11 (86.89)	33.58±1.37 (95.7)	14.5±0.35 (90.54)	75.48±1.38 (78.79)	60.57±0.33 (99.9)
11	914±16.67 (85.14)	0.33±0.02 (93.99)	18.12±0.2 (96)	56.67±0.2 (71.20)	33.97±0.3 (68.94)	1138.3±7 (93.6)	61.28±1.62 (93.9)	20.78±0.87 (90.54)	62.33±0.1 (83.32)	83.17±1.9 (95.4)
12	38.83±0.25 (60.39)	2.14±0.05 (61.25)	14.64±0.15 (71.2)	52.24±0.42 (95.3)	32.3±0.18 (83.68)	619.96±8.25 (76.54)	54.36±1.39 (98)	152.25±1.67 (84.02)	63.148±0.86 (94.35)	361.5±2.5 (83)
13	26.81±0.36 (69.26)	1.33±0.02 (97.12)	14.06±0.28 (75.6)	56.33±0.91 (84.78)	3.72±0.85 (84.41)	670.1±28.6 (97.23)	60.83±1.57 (79.3)	66.92±0.72 (95.99)	64.66±0.26 (95.30)	125.83±3.83 (91.5)
14	88.53±2.77 (87.9)	2.62±0.03 (94.23)	9.68±0.22 (72.4)	34.7±0.97 (89.73)	22.45±0.5 (66.07)	632.2±22 (99)	32.87±1.17 (100)	229.30±1.97 (95.05)	49.53±1.23 (90.51)	131.62±4.65 (94)
15	1208±41.67 (96.64)	15.5±0.31 (89.86)	303.92±4.17 (94.9)	53.20±0.71 (70.78)	164.88±1.38 (89.4)	5440.8±73 (97.18)	195.75±4.33 (95.3)	5062±20.83 (88.16)	63.80±2.07 (91.09)	8275±66.67 (95.5)

*Numbers in brackets are extraction of efficiency

completely solved by the Aqua regia solution [45]. 90% of manganese, Zn, Cu, Pb and Cd of the entire soil can be extracted by the Aqua regia solution [12]. 95% of soil total zn, Cu, Ni about 80% of soil total Cd and about 60% of soil total Cr can be extracted by Aqua regia [22, 39].

Table 9 shows the amount of heavy metals in 15 soil samples obtained by the EPA 3050B method. The efficiency of extraction of this method for As was different between 37.61 and 97.72%. The efficiency of Cd extraction was between 60.25 and 96.34%. The extraction efficiency was different between 46.32–72.46, 47.61–71.66, 44.84–86.55, 49.21–76.64, 76.95–96.73, 43.38–99.9, 43.17–81.12, and 45.83–72.69%, respectively, for the Co, Cr, Cu, Mn, Ni, Pb, V and Zn elements. The low extraction efficiency of samples 5, 3, 1, 13, 12 and 14 is likely caused by high clay content. The low extraction percentage in samples 5, 4, 12, 8, 13 and 1 is related to the high organic matter content of the soil. Low estimation of Pb according to EPA 3050B method in soil No. 1 and Nos. 12–15 is related to the lead in lead sulfide (PbS) form, which nitric acid causes oxidation of PbS, that results in salt formation of $PbSO_4$, which has low solubility and remains in sediment form. In contrast, HCl in the Aqua regia media tends to form a lead chloride complex ($PbCl_2$) in the ISO 11466 method, which is a soluble compound and easily extracted [38]. In general, the EPA 3050B was less effective than most of the elements in the ISO 11466 method. Peña-Icart et al. [38] reported that in six sediment samples examined by EPA 3050B and ISO 11466, the extraction efficiency of Co, Ni and Pb is higher in the ISO 11466 method. The extraction percentage was reported between 97–100% for Cd, Cr, Ni, Pb and Zn in both soil samples and sewage sludge [47]. The EPA 3050B method has high efficiency in the extraction of Cd, Ni, Co, Pb and Zn from soil [49].

3.6 Correlation between Heavy Metals Concentration in Soil

The result correlation between the concentrations of heavy metals is shown in Table 10. As it is clear, there is a strong and significant correlation between As–Co, As–Mn, As–Pb and As–Zn, Co–Cd, Co–Cu, which is related to the geological origin of these metals. These metals are present in most geological formations in the structure of minerals. There is a positive and significant correlation between Cr and Ni, which is likely due to these two elements in the geological formations in chromite ($FeCr_2O_4$) and millerite (NiS) forms. There is a positive and significant correlation between Cu–As, Cu–Cd, Cu–Co, Cu–Mn, Cu–Pb, Cu and Zn. There is a positive and significant correlation between manganese and As, Cd, Co, Pb and Zn with coefficients of 0.69, 0.8, 0.89, 0.97 and 0.98, respectively. There is a positive and significant relationship (0.98) between Pb and Zn

which is caused by these two elements in Anguran geological formation in Zanjan and the Lakan lead and zinc mine in Markazi province, Iran, in the form of anglesite ($PbSO_4$), cerussite ($PbCO_3$), smithsonite ($ZnCO_3$) minerals. There is an insignificant negative relationship between V and most of the measured elements. There is a positive and significant correlation between Ni, Cu, Cr, Zn and Cd in 295 soil samples analyzed in grassland, forests and agriculture soils in Ireland [33].

3.7 Correlation between percentage of heavy metals recovery and soil characteristics

Pearson correlation coefficient (r) between extractable metals by two pseudo-total digestion methods including ISO-11466 and EPA 3050B and soil properties including percentage of clay, organic matter, $CaCO_3$, pH and EC, as well as the correlation coefficient between heavy metals (Tables 11 and 12) was used to predict the effect of soil features on the percentage of soil heavy metals recovery. Clay and soil organic matter has a negative with the extraction of heavy metals from the soil, but this is not significant for most of the elements. The percentage of clay has a negative and significant effect on the recovery of zinc extracted according to the ISO-11466 method. Also, the EPA 3050B method showed a negative and significant effect on nickel element retrieval. The amount of organic matter has a negative and significant effect on soil arsenic recovery in ISO 11466 and on the recovery of nickel in the EPA 3050B. Heavy metals bound with soil particles and have high tend to form a bond with soil organic matter, which causes reduction in its extraction by extracting solution extractor [54]. $CaCO_3$ content is one of the most important factors that control the accumulation, mobility and bioavailability of heavy metals in arid soils [34].

The results showed that lime percentage had negative relationship with heavy metal extraction, but this effect was not significant for most of the elements except recovered Co by the ISO-11466 method, which is consistent with the results obtained in Sects. 3–4. There is a negative correlation between soil pH and As, Cd, Co, Cu, Mn, Pb and Zn. The pH of the soil keeps the metals in the soils through several mechanisms. Many of the adsorption sites in soil are pH dependent, i.e., Fe and Mn oxides, organic matter, carbonate and clay minerals [34]. Reducing the extraction of heavy metals by increasing soil pH might be explained by lowering solubility at high pH and decomposition of minerals and/or organic-mineral complexes. There is an insignificant and positive relationship in terms of the amount of heavy metals between the soil and soil EC, except for recovered zinc element using the EPA 3050B method, which is significant. There is a close relationship between the amount of metals extracted by EPA

Table 9 The concentration of heavy metals (mg kg^{-1}) in 15 soils analyzed by EPA 3050B (mean ± standard deviation) ($n = 2$)

Soil number	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	V	Zn
1	31.38 ± 0.4 (57.14)	5.51 ± 0.07 (63.25)	18.81 ± 0.38 (70.12)	69.2 ± 1.57 (68.6)	59.23 ± 0.68 (86.55)	1767 ± 6.5 (57.53)	120.98 ± 1.22 (80.39)	1213 ± 16 (54.7)	64.28 ± 1.2 (57.2)	2418.5 ± 15.5 (48.24)
2	4 ± 0.15 (97.72)	0.2 ± 0.03 (93.02)	14.43 ± 0.27 (49.50)	32.54 ± 1.49 (49.82)	28.1 ± 2.54 (49.90)	651.4 ± 18.6 (59.73)	20.72 ± 0.45 (94.46)	17.9 ± 0.7 (63.96)	205 ± 6.95 (62.4)	60.93 ± 0.73 (53.94)
3	10.28 ± 0.5 (37.61)	0.13 ± 0.015 (90.59)	3.5 ± 0.26 (55.85)	15.1 ± 0.16 (57.65)	17.91 ± 0.26 (44.84)	151.9 ± 0.7 (67.84)	17.7 ± 0.35 (81.20)	5.68 ± 0.1 (43.38)	23.5 ± 0.4 (66)	21.23 ± 0.7 (49.37)
4	9.6 ± 0.2 (47.94)	0.28 ± 0.025 (88.89)	8.37 ± 0.1 (52.97)	36.7 ± 0.2 (57.6)	54.81 ± 0.1.19 (67.93)	462.2 ± 5.4 (71.21)	45.65 ± 0.3 (83.17)	32.1 ± 0.29 (62.81)	38.78 ± 0.52 (53.42)	55.92 ± 0.5 (64.93)
5	26.75 ± 0.1 (61.18)	5.1 ± 0.04 (88.9)	13.63 ± 0.14 (63.42)	37.598 ± 0.12 (68.85)	54.16 ± 1.76 (78.6)	984.45 ± 7.1 (76.64)	37.55 ± 0.4 (76.95)	43.74 ± 0.59 (73.15)	62.83 ± 0.4 (60.55)	190.4 ± 0.6 (72.69)
6	11.27 ± 1.43 (41.94)	0.17 ± 0.05 (85)	9.24 ± 0.1 (52.77)	22.87 ± 0.17 (48.8)	35.3 ± 0.1 (81.47)	635.2 ± 5.4 (75.24)	30.25 ± 0.95 (92.17)	200.85 ± 1.65 (69.45)	54.4 ± 0.62 (53.54)	52.93 ± 0.43 (64.23)
7	16.8 ± 0.49 (55.1)	11.2 ± 0.05 (83.83)	19.2 ± 0.6 (63.18)	154.3 ± 4.4 (53.12)	62.6 ± 1.57 (73.54)	546.5 ± 12.9 (49.21)	356.3 ± 3.7 (86.9)	11.5 ± 1.46 (72.66)	90.34 ± 4 (43.17)	40.85 ± 0.8 (57.14)
8	5.6 ± 0.28 (76.89)	0.14 ± 0.02 (75.68)	40.1 ± 0.74 (63.72)	345.95 ± 0.45 (61.3)	32.8 ± 0.63 (72.02)	570.8 ± 4.1 (65.7)	925.6 ± 4.75 (81.84)	15.85 ± 0.61 (84.91)	448.54 ± 0.26 (61.7)	30.38 ± 0.31 (45.83)
9	13.29 ± 1.4 (72.72)	0.8 ± 0.05 (87.36)	17.81 ± 0.52 (64.98)	96.44 ± 1.92 (64.25)	73.91 ± 0.62 (85.98)	605.3 ± 5.6 (74.89)	175.23 ± 0.85 (93.46)	13.9 ± 0.7 (76.05)	79.5 ± 2 (64.6)	49.74 ± 1.95 (64.55)
10	20.66 ± 0.77 (79.2)	0.16 ± 0.02 (95.29)	7.9 ± 0.12 (46.32)	24.34 ± 0.2 (60.88)	22.87 ± 0.36 (63.2)	270.4 ± 0.2 (62.33)	32.63 ± 0.85 (93.03)	13.83 ± 0.15 (86.11)	49.5 ± 0.13 (51.64)	41.68 ± 0.61 (68.77)
11	577.1 ± 1.85 (53.75)	0.32 ± 0.05 (88.73)	10.4 ± 0.1 (55)	38.2 ± 0.23 (48)	31.68 ± 0.52 (64.29)	765.1 ± 4.35 (62.92)	47.52 ± 0.22 (90.27)	18.1 ± 0.92 (70.25)	44.67 ± 0.31 (59.71)	48.5 ± 0.35 (55.66)
12	32.63 ± 0.9 (50.74)	2.1 ± 0.02 (60.25)	9.7 ± 0.1 (47.2)	38.8 ± 0.5 (70.73)	28.92 ± 0.71 (74.92)	454.5 ± 1.25 (56.1)	47.52 ± 0.14 (85.64)	115.2 ± 3.9 (63.58)	50 ± 0.15 (74.73)	243.25 ± 0.5 (55.88)
13	25.44 ± 0.4 (65.73)	1.32 ± 0.05 (96.34)	11.1 ± 0.14 (59.73)	45.91 ± 0.72 (69.1)	30.71 ± 1.26 (84.38)	514.7 ± 2.8 (74.69)	67.25 ± 0.26 (87.64)	63.9 ± 0.5 (91.66)	55.04 ± 0.69 (81.12)	91.95 ± 0.66 (66.89)
14	72.73 ± 1.61 (72.21)	2.62 ± 0.14 (94.25)	7.37 ± 0.14 (55.2)	27.71 ± 0.25 (71.66)	24.1 ± 0.11 (70.8)	442.35 ± 0.1 (69.28)	31.8 ± 0.95 (96.73)	241 ± 4 (99.9)	40 ± 0.26 (72.94)	89.1 ± 0.72 (63.58)
15	1090 ± 10 (87.2)	15.48 ± 0.3 (89.74)	232 ± 5.7 (72.46)	35.78 ± 0.54 (47.61)	135.3 ± 2.4 (73.4)	3337.5 ± 57.5 (59.61)	195.2 ± 0.25 (95.03)	4894 ± 31 (85.22)	41.1 ± 1.4 (58.68)	6253.5 ± 35.7 (72.24)

*Numbers in brackets are extraction of efficiency

Table 10 Correlation coefficient (*r*) of Pearson between heavy metal concentrations measured by ISO-14869-1

Parameter	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	V	Zn
As	1									
Cd	0.45	1								
Co	0.72**	0.7**	1							
Cr	−0.13	0.07	0.07	1						
Cu	0.61*	0.78**	0.87**	0.02	1					
Mn	0.69**	0.8**	0.89**	−0.03	0.85**	1				
Ni	−0.06	0.10	0.19	0.98**	0.07	0.06	1			
Pb	0.67**	0.76**	0.92**	−0.10	0.83**	0.97**	0.01	1		
V	−0.21	0.09	−0.09	0.11	0.07	−0.01	−0.002	−0.14	1	
Zn	0.61*	0.76**	0.85**	−0.09	0.79**	0.98**	0.01	0.98**	−0.12	1

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

Table 11 Correlation coefficient (*r*) of Pearson between chemical and physical properties of soil and percent recovery of heavy metals measured by ISO-11466 method

Parameter	Clay (%)	OC (%)	CaCO$_3$ (%)	pH	EC	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	V	Zn
Clay (%)	1														
OC (%)	0.64**	1													
CaCO$_3$ (%)	0.53*	0.20	1												
pH	0.26	0.24	0.38	1											
EC	−0.38	−0.22	−0.30	−0.86**	1										
As	−0.48	−0.6*	−0.26	−0.19	0.44	1									
Cd	−0.09	−0.22	0.02	0.13	0.03	0.45	1								
Co	−0.47	−0.36	−0.73**	−0.22	0.22	0.57*	0.06	1							
Cr	0.003	−0.15	−0.08	0.15	−0.33	−0.14	−0.46	0.04	1						
Cu	0.12	0.04	−0.41	−0.33	0.33	0.05	−0.13	0.15	0.20	1					
Mn	−0.30	−0.12	0.19	0.21	0.19	0.45	0.57*	−0.004	−0.36	−0.26	1				
Ni	−0.39	−0.17	0.12	0.07	0.12	0.15	−0.08	−0.17	−0.26	−0.41	0.10	1			
Pb	−0.42	−0.10	−0.22	0.10	0.01	0.12	0.19	−0.03	0.06	−0.34	0.47	0.12	1		
V	−0.14	−0.48	0.09	−0.12	0.09	0.29	−0.18	−0.02	0.30	−0.07	0.08	−0.11	0.30	1	
Zn	−0.56*	−0.08	−0.32	−0.04	0.26	0.18	0.29	0.23	−0.22	−0.20	0.42	0.41	0.39	−0.23	1

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

3050B and ISO 11466 methods with physical and chemical properties of soil, and as a result, inconsistent results have been reported in environmental studies [21]. Therefore, the results indicate that different chemical and physical properties of soil should be considered during digestion of heavy metals of soil using partial digestion methods.

3.8 Recommendation of digestion method

The results in the present study show a significant correlation between the total digestion method (ISO-14869) and pseudo-total digestion (ISO 11466 and EPA 3050B) in all soils (P < 0.05). Silicate minerals are affected by the reaction of HF with Si to form the gaseous SiF$_4$. HClO$_4$ is a powerful oxidizer and dehydrating agent. The HNO$_3$ is used to prevent the explosive reactions of the soil organic matter with HClO$_4$ using in the ISO-14869 method. For As, Co and Pb, there is a very strong correlation ($R^2 = 1$) between ISO-14869 and ISO-11466. For the rest of the elements, there was a high correlation between these two methods. The EPA3050B method showed high correlation for most of the elements by the ISO-14869 method, and for only the Zn element of this correlation was slightly low ($R^2 = 0.982$). Based on QA/QC results, ISO11466 or Aqua regia can be used to analyze heavy metals in soil. However, the ISO-14869 method is a good method for baseline studies in soil, but it is good with the cost and volume of more consumed acid (Table 13).

Table 12 Correlation coefficient (r) of Pearson between chemical and physical properties of soil and percent recovery of heavy metals measured by EPA 3050B method

Parameter	Clay (%)	OC (%)	CaCO$_3$ (%)	pH	EC	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	V	Zn
Clay (%)	1														
OC (%)	0.64**	1													
CaCO$_3$ (%)	0.53*	0.20	1												
pH	0.26	0.24	0.38	1											
EC	−0.38	−0.22	−0.30	−0.86**	1										
As	−0.49	−0.26	−0.47	−0.29	0.24	1									
Cd	−0.21	−0.16	0.17	0.06	0.12	0.29	1								
Co	0.12	0.10	−0.25	−0.39	0.49	0.08	−0.15	1							
Cr	0.68**	0.55*	0.26	0.16	−0.37	−0.02	−0.30	0.03	1						
Cu	0.22	0.33	−0.45	−0.04	0.06	−0.09	−0.35	0.49	0.41	1					
Mn	0.34	0.48	0.27	0.44	−0.15	−0.13	0.44	−0.02	0.24	0.23	1				
Ni	−0.59*	−0.69**	−0.25	−0.21	0.29	0.49	0.44	−0.22	−0.34	−0.08	−0.06	1			
Pb	−0.28	−0.02	−0.32	−0.24	0.27	0.55*	0.40	0.13	0.18	0.35	0.18	0.52*	1		
V	0.43	0.19	0.43	0.05	−0.11	0.10	−0.001	−0.12	0.57*	0.07	0.35	0.06	0.22	1	
Zn	−0.16	0.09	−0.29	−0.57*	0.7**	0.21	0.47	0.20	−0.12	0.27	0.27	0.38	0.52*	−0.04	1

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

4 Conclusions

Concentration of heavy metals (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, V and Zn) using ICP-OES and GFAAS and three methods of acid digestion with different acid composition (including HNO$_3$, HCl, H$_2$O$_2$, HClO$_4$ and HF) were measured in two reference materials and 15 soil samples. Using acid digestion methods is needed to quantify the amount of heavy metals in solid samples such as soils, sediments and sewage sludge. The use of quality control tools such as certified reference materials is a key factor to additional assures the accuracy of the results. This study specifies the importance of validating sample digestion methods using reference materials and soil samples before environmental analyzes. Using HF and HClO$_4$ in the digestion process increases the extraction and recovery of heavy metals from the soil. However, using HF and HClO$_4$ for routine analyzes is not recommended because the digestion process is hazardous and difficult, and also it is required to have certain laboratory equipment (for example, a washable perchloric hood) due to its high explosive potential and the corrosive nature of HClO$_4$. For the digestion procedure, the extraction time and the total reagent consumption have significant importance. In ISO 14869-1, the amount of acid used is about 25 ml, considering the repeat steps, and about 6 h is required to complete the digestion. In EPA 3050B, the samples were extracted for 180–200 min including evaporation and cooling. Depending on the repetition of the HNO$_3$ addition step, the reactant volume is different between 50 and 35 ml. In the ISO 11466 method, about

Table 13 Correlation of linear regression ($Y = X0 + aX$) of heavy metal content by different digestion methods in the soils

Y	Element (sample nos.)	a (coefficient of X)	X_0	R^2
ISO-14869	As ($n = 15$)	1.02	16.5[a]	1.00**
		1.26	31.02[b]	0.99**
ISO-14869	Cd ($n = 15$)	1.14	0.058[a]	0.998**
		1.16	0.17[b]	0.991**
ISO-14869	Co ($n = 15$)	1.04	2.27[a]	1.00**
		1.36	4.64[b]	1.00**
ISO-14869	Cr ($n = 15$)	1.03	12.49[a]	0.994**
		1.65	2.12[b]	0.995**
ISO-14869	Cu ($n = 15$)	1.06	8.28[a]	0.99**
		1.25	5.95[b]	0.977**
ISO-14869	Mn ($n = 15$)	1.05	24.96[a]	0.996**
		1.71	−92.97[b]	0.995**
ISO-14869	Ni ($n = 15$)	1.12	−3.87[a]	0.999**
		1.22	−6.65[b]	0.999**
ISO-14869	Pb ($n = 15$)	1.13	14.46[a]	1.00**
		1.13	67.59[b]	0.999**
ISO-14869	V ($n = 15$)	1.09	5.66[a]	0.995**
		1.66	1.27[b]	0.966**
ISO-14869	Zn ($n = 15$)	1.34	−42.80[a]	0.997**
		1.95	−59.63[b]	0.982**

**Correlation is significant at the 0.01 level ($P < 0.01$)

[a] (X = the ISO 11466 method)

[b] (X = the EPA 3050B method)

19 h is required to complete the digestion process with a 16-h start-up time and the volume of the used reagent is 28 ml. Depending on the elements studied, the digestion method should be selected according to the recovery results in the reference material and the results of the natural samples. The low extraction efficiency for some elements is likely caused by binding the metals with silicate clays in the soil, which is extracted lower by the acids used in these two methods. In this study, the ISO 11466 or Aqua regia method will be considered as a suitable method considering all factors such as extraction efficiency, the amount of used acid and the required equipment in reference samples and calcareous soils, if digestion of all the elements is not required. The Aqua regia method is a suitable method for routine analysis, which is not required to use expensive tools and devices such as platinum tubes, PTFE digestion tubes or digestion bombs, and other special tools compared to other digestive methods like using $HClO_4$ and HF. In high-lime soils, adding Aqua regia solution, high foaming causes problem that will be eliminated by adding additional HNO_3 before the heat treatment begins. The results showed that lime in calcareous soils does not affect the recovery of elements. Also, the results showed that there is a positive and significant correlation between the measured heavy elements, indicating that most of the elements in the structure of minerals are geologically located.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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