

Microwave-Assisted Digestion Procedures for Total Lead and Cadmium Content Determination in Copșa Mică Soils

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The aim of the study was to establish the best method of digestion for determination of total content of certain heavy metals (Cd and Pb) in Copșa Mică soils using different microwave-assisted digestion procedures. Five digestion procedures using various acid combinations (HCl, HF and HNO₃) and volumes were tested, using two Certified Reference Materials (CRMs) and two polluted soil samples collected from Copșa Mică. Cadmium and lead content in the digests were analyzed using Flame Atomic Absorption Spectrometry (FAAS). The analytical performance parameters and recoveries showed that all five applied digestion procedures are suitable for the determination of total Cd and Pb content in polluted soils, but the best digestion procedure for Cd analysis in present case was the adapted EPA 3052 procedure with a mixture of nitric and hydrofluoric acid, while for Pb is the adapted ISO 11466 procedure with aqua regia.

Keywords: microwave digestion, soil, heavy metals, FAAS

Impact of human activities on soil quality has increased over the years, mainly due to extensive exploitation of natural resources and polluting industries development. As a result, soil and subsoil have been contaminated with various pollutants, mainly heavy metals and organic substances, resulting in the emergence and development of contaminated sites, affecting human health and environment. One of these polluted sites is Copșa Mică, and the investigations performed during the last years have demonstrated that heavy metals [1-4], especially Cd and Pb, are still present, even if the smelting activity has ceased. The highest amounts of Pb and Cd are to be found in the soil upper horizons. The total contents of lead and cadmium in the vicinity of the former smelter largely exceed the alert and intervention thresholds stated by Romanian laws [5] (Pb of 5.61 up to 27.68 times and Cd of 5.99 up to 133.3 times) [6]. Increasing the distance from the source, the pollution intensity decreases and the concentration of metals is below the threshold for intervention, but higher than normal values [7].

For the determination of the total amount of heavy metals in soil, most methods require the wet digestion of the sample, usually by means of oxidizing acids. The use of concentrated HNO₃ in a closed system under elevated temperatures and pressure is documented since 1860 [8]. Because sometimes nitric acid alone is not strong enough to convert organic molecules to CO₂ and H₂O (complete oxidation), in many cases other acids, like HCl and/or HF, or H₂O₂ are required [9]. To avoid erroneous results and unnecessary use of hazardous extraction agents it is important to evaluate the existing digestion procedures [10].

ISO 11466 describes a method for the digestion with aqua regia for trace elements determination from soils and similar materials that contain less than 20 % (m/m) organic carbon.

Materials containing more than 20% (m/m) organic carbon will require treatment with additional nitric acid.

The resulting clear solution is suitable for the determination of trace elements using appropriate atomic spectrometric techniques [11].

EPA Method 3051A is a digestion procedure that does not intend to accomplish total decomposition of the sample. It is applicable to the microwave-assisted acid extraction/dissolution of sediments, sludges, soils, and oils digestion of sediments [12].

EPA Method 3052 is another microwave-assisted digestion procedure designed for digesting siliceous and organic based matrices. In this method, hydrofluoric acid (HF) is added at varying concentrations depending on the silicon dioxide (SiO₂) concentration in the sample. All these digestion methods clearly describe the microwave digestion device requirements, as well as their chemistry, reaction temperature, time a.s.o. [13].

The primary aim of this research was to ascertain which is the most appropriate digestion method for determination of total metal content (Cd and Pb) in Copșa Mică polluted soils, using different microwave-assisted digestion procedures. To achieve this goal, soil samples (2 CRMs and 2 polluted soil samples from Copșa Mică) have been digested, according to ISO 11466/SR EN 13346, EPA Method 3051A and EPA Method 3052 using the microwave digestion system in a TOPwave digester, with various acid (HCl, HF and HNO₃) combinations and volumes.

Experimental part

Samples

Two mean soil samples (n=20) were collected from Copșa Mică, one near the former smelter, SOMETRA S.A. (N 46° 6' 45.61", E 24° 14' 27.10" - Soil sample 1) and the other from a place situated approximately 4 km eastwards from pollution source (N 46° 7' 0.60", E 24° 16' 48.69" - Soil sample 2). Soil samples were collected at 0-20 cm depth and stored in new polyethylene bags for transport to laboratory, where they have been characterized, with the results presented in table 1.

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Soil sample	pH	Organic carbon %	Humus %	Sand %	Silt %	Clay %	Soil texture
1	5.68	0.81	1.40	73.2	9.8	17.0	Sandy loam
2	6.24	1.276	2.20	70.5	12.3	17.2	Sandy loam

Table 1
SOIL CHARACTERISTICS OF RESEARCH SITES (0-20 CM DEPTH). ALL RESULTS ARE MEAN VALUES OF THREE INDEPENDENT DETERMINATIONS, REPORTED TO DRY WEIGHT

Soil pH was measured in a 1:5 soil/water suspension using a HI 253 pH/ mV/ Ion and temperature bench meter from Hanna Instruments (USA). Organic carbon content was determined under heating with a potassium dichromate/sulfuric acid mixture and the humus content was calculated by multiplying the percentage of organic carbon by 1.724 (STAS 7184/21-82). Kubiena pipette method was used to determine the percentages of sand, silt, and clay in the soil and a soil textural triangle was used to determine soil textural class.

For determining the total content of metals in soil extracts, all soil samples were air dried, powdered, and dried at 105°C to constant weight. Each sample was sieved to less than 2 mm sieve and then ground and sieved to a fine powder (65µm) using a Vibratory Sieve Shaker/Micro Mill Pulverisette 0, manufactured by Fritsch Co., Germany.

Samples were accurately weighted to approximately 0.2500 - 0.3000 g directly in microwave vessels using a precise analytical balance *Partner As220/C/2* with internal calibration.

To determine total cadmium and lead content, the fraction below 65µm was digested using a TOPwave microwave digestion system from Analytik Jena, Germany, according to five different microwave-assisted digestion procedures, using HNO₃, HNO₃-HF, HNO₃-HCl- HF, according to EPA 3051 A, EPA 3052 and ISO 11466/EN 13346 [14], respectively.

The resulting solutions were filtered through quantitative filter discs (grade 391, Filtrak), then diluted with ultra pure water to 100 mL in volumetric flasks, and stored at 4°C for analyses.

Microwave PTFE Teflon vessels were carefully cleaned before each digestion using a washing procedure for vessel (9 mL HNO₃ and 1 mL HCl, 200 °C, 40 bar, 20 min).

The extracts were analyzed using a ContraAA 700, Flame Atomic Absorption Spectrometer, manufactured by Analytik Jena, Germany.

Reagents

To validate the digestion procedures, two certified reference materials: 7001 - Light Sandy Soil with normal analyte levels, from Analytika Co. Ltd. Czech Republic, and Standard Reference Material Gleba S-1, Krakov, Poland were used. The first, with particles smaller than 100µm is certified for total element contents and contents of element fraction extractable by conventional procedure in soil and materials of similar matrix [15]; the second, having a particle size less than 0.15 mm is also certified for total element contents [16].

Among the concentrated acids used, 65% (w/v) HNO₃ and 35% (w/v) HCl were provided by Merck (Darmstadt, Germany), 40% (w/v) HF was purchased from Chimreactiv (Bucharest, Romania).

The calibration standard solutions for Cd and Pb were prepared using Scharlau, Spain, standard solutions with a purity of 997 mg/L.

Ultrapure water (conductivity below 0.055 µS/cm) was obtained using a TKA Smart2Pure water purification system, manufactured by Thermo Electron LED GmbH, Stockland, Germany.

Microwave-assisted digestion procedures

Soils were digested using the TOPwave microwave digestion system and a combination of HNO₃, HF and HCl at different ratios of acids and different parameters (temperature, pressure, power, time, etc.)

Five digestion procedures using various acid combinations of hydrochloric acid, nitric acid and hydrofluoric (HCl, HNO₃ and HF) and volumes were applied to certified samples to provide the most appropriate method for determination of Cd and Pb in soils. Basically, these five digestion procedures differ in the type of acid mixtures and the microwave temperature programs used (tables 3-5).

Element	CRM 7001-Light Sandy Soil		CRM Soil S-1
	Total element content µg/g d.w.	Content of element fractions extractable by aqua regia µg/g d.w.	Content (confidence limit 95%) µg/g d.w.
Cd	0.32 ± 0.05	0.29 ± 0.04	0.30 ± 0.08
Pb	43.80 ± 3.70	24.10 ± 1.70	15.00 ± 3.60

Table 2
CONCENTRATIONS OF ELEMENTS RECOMMENDED AS REFERENCE VALUES IN CERTIFIED REFERENCE MATERIAL (CRM) 7001-LIGHT SANDY SOIL [15] AND CERTIFIED REFERENCE MATERIAL SOIL S-1, DRY WEIGHT (D.W.) [16]

Procedure 1. Aqua regia (3 mL HNO ₃ ; 9 mL HCl), adapted ISO 11466 method. Total time: 65 minutes					
Step	T (°C)	P (bar)	Power (%)	Ramp (min.)	Time (min)
1	140	40	90	8	15
2	50	0	0	8	50

Table 3
MICROWAVE-ASSISTED DIGESTION CONDITIONS USED IN DIGESTION PROCEDURE 1

Procedure 2. Aqua regia (2.5 mL HNO ₃ ; 7.5 mL HCl), adapted EPA 3051 A method. Total time: 32 minutes					
Step	T (°C)	P (bar)	Power (%)	Ramp (min.)	Time (min)
1	175	40	80	1	10
2	50	0	0	4	22

Table 4
MICROWAVE-ASSISTED
DIGESTION CONDITIONS
USED IN DIGESTION
PROCEDURE 2

Procedure 3. 10 mL HNO ₃ only, adapted EPA 3052 method. Total time: 42 minutes					
Procedure 4. 10 mL HNO ₃ ; 2 mL HF, adapted EPA 3052 method. Total time: 42 minutes					
Procedure 5. 9 mL HNO ₃ ; 3 mL HCl; 1 mL HF, adapted EPA 3052 method. Total time: 40 minutes					
Step	T (°C)	P (bar)	Power (%)	Ramp (min.)	Time (min)
1	180	50	90	6	10
2	50	0	0	4	30

Table 5
MICROWAVE-ASSISTED
DIGESTION CONDITIONS
USED IN DIGESTION
PROCEDURES 3, 4 AND 5

Digestion procedure 1. Aqua regia (HNO₃/HCl) – a modified version of ISO 11466:1995/EN 13346 adapted for soil digestion with aqua regia using an Analytik Jena microwave digestion system was applied. A representative sample of approximately 0.25 g soil was accurately weighed directly into the microwave digestion vessels and 12 mL of aqua regia (HNO₃:HCl = 1:3) were added and the mixture was carefully stirred with a clean glass bar. Samples were then heated in the microwave oven with the program indicated in table 3. The main parameters of this program were chosen basically in agreement with manufacturer recommendations, but also taking into account previous studies on microwave-assisted digestion optimization [17].

After cooling, the samples were filtered through filter papers to remove any undigested solid material. The filtrate was collected in 100 mL volumetric flasks. The filter and the residue were rinsed with 0.5% (v/v) HNO₃ and the solution was then brought to 100 mL with 0.5% (v/v) HNO₃ and analyzed by FAAS method.

Digestion procedure 2. HNO₃/HCl (adapted EPA 3051A- microwave assisted acid digestion recommended for sediments, sludge, soils, and oils). A modified version of the EPA method 3051A protocol for HNO₃/HCl digestion was used in this procedure. A representative sample of 0.25 g soil, 7.5 mL concentrated HNO₃ and 2.5 mL concentrated HCl have been added in the microwave digestion system and heated following the program from table 4. Thereafter, the procedure was similar to the modified ISO 11466 procedure, described above, but with a smaller volume of reagent.

Digestion procedure 3. HNO₃ only (adapted EPA 3052 – microwave assisted acid digestion procedure recommended for siliceous and organically based matrices). As before, a representative sample of 0.25 g was weighed and mixed with 10 mL concentrated HNO₃ and then digested following the program presented in table 5. Because the procedures 4 and 5 have been performed in the same conditions, only the oxidizing agents differing, they are also presented in table 5.

Digestion procedure 4. HNO₃/HF – a modified version of the microwave-assisted EPA method 3052 protocol adapted for digestion of soil - with a mixture of nitric acid (10 mL HNO₃) and hydrofluoric acid (2 mL HF) using the same microwave digestion program as in digestion procedure 3, indicated in table 5. Hydrofluoric acid was added to ensure that all aluminosilicates present were completely dissolved in the microwave digestion system.

Digestion procedure 5 - HNO₃/HCl/HF. This is an adapted procedure from EPA 3052 method, with a mixture of nitric acid (9 mL HNO₃), hydrochloric acid (3 mL HCl) and hydrofluoric acid (1 mL HF) using the same microwave digestion program as for digestions procedures 3 and 4 (table 5).

Instrumentation

Microwave-Assisted Digestion System

A TOPwave microwave-assisted pressure digestion system from Analytik Jena, Germany, was used to digest the samples. The microwave digestion system is equipped with an 8-position rotor (CX100) and self-regulates its power to reach and maintain specified pressure and temperature (max. pressure 100 bar and max. temperature 230 °C). This last parameter was controlled by a sensor placed into one of the vessels.

Flame atomic absorption spectrometer (FAAS)

For determination of Cd and Pb in soil samples it was used a High-Resolution Atomic Absorption Spectrometer (HR-CS AAS) with a high-intensity Xe short-arc lamp as continuum source (ContraAA700 from Analytik Jena, Germany). An AS 52s Autosampler was used for sample uptake and for dilution and an Injection Module (SFS 6) which allowed washing or continuous aspiration of the carrier solution, thus keeping the burner at a constant temperature by the aerosol [18]. Specific parameters recommended by manufacturer for the determination of Cd and Pb were applied, the absorbance measurements being performed using the spectral lines for Cd at 228.8 nm and for Pb at 217.0 nm [19].

The linearity of calibration curves for the expected range concentration of Cd and Pb in soil samples was verified and, as expected, a very good linearity was obtained for Cd in the range of 0 - 1.2 mg/L (R² = 0.9998) and for Pb in the range 0 - 4 mg/L (R² = 0.9989).

Results and discussions

To establish which is the effect of acid combination used to mineralize the soils, and therefore which is the most appropriate digestion procedure, the soil samples were digested and analyzed in triplicates for each procedure and percent recoveries of Cd and Pb for two CRMs soils were calculated for all five microwave-assisted digestion procedures. This calculation was done by dividing the obtained values to the certified total values and then by multiplying the results with 100. Both CRMs were digested

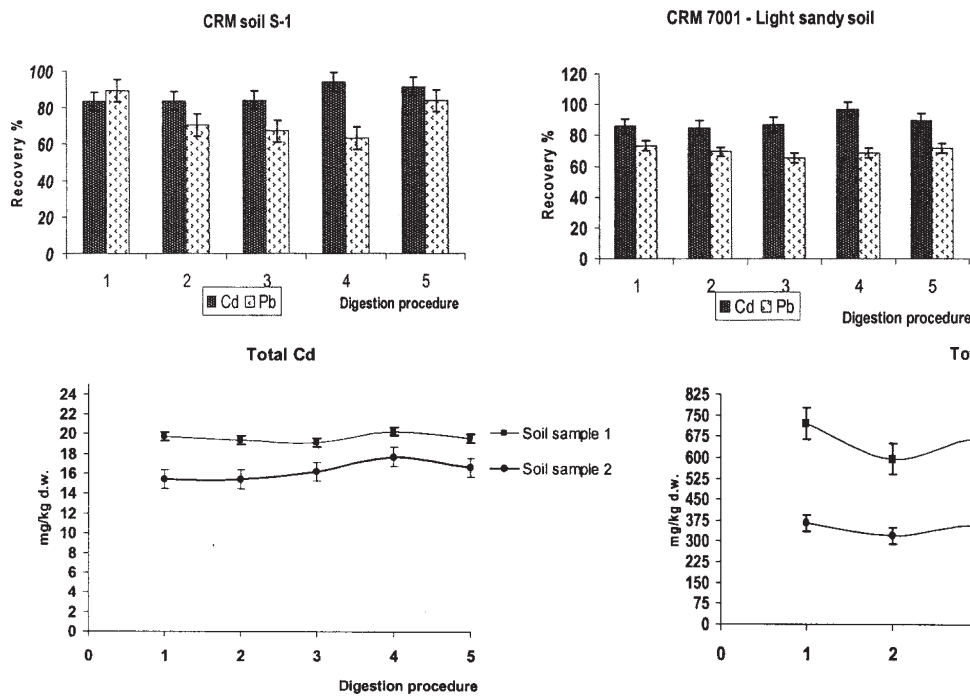


Fig.1. Percent recovery (%) of Cd and Pb from soil CRMs using five microwave-assisted digestion procedures 1-5

Fig. 2. Heavy metal content (mg·kg⁻¹, d.w.) in two Copșa Mică soil samples by 5 different digestion procedures. Each value represents the mean for three determinations.

and the percentage recoveries were compared to the certified values of the CRM. The results are represented in figure 1.

From figure 1 it can be seen that good percentage recovery has been obtained for Cd and Pb in CRMs (63.12±8.92% up to 96.92±5.52%), all five digestions procedures giving results in concordance with their respective certified values, but with slight differences.

The 3 mL HNO₃ - 9 mL HCl mixture used in Digestion procedure 1 (adapted from ISO 11466 method, 140°C, 40 bar) gave good recovery for Pb in CRM soil S1, 88.93 ± 6.92%, and not so good for CRM-7001, 73.38 ± 3.21% respectively. Applying this procedure to Cd determination, very good results were obtained, the recovery being greater than 80% for both soils.

Procedure 2, adapted from EPA from 3051 A method (2.5 mL HNO₃:7.5 mL HCl, 175 °C) and Procedure 3, adapted from EPA 3052 method (10 mL HNO₃ only, 180 °C, 50 bar) gave good recoveries for Cd (>82%) but not the best for Pb, where the recovery is less than 75 % for both CRMs.

The digestion procedure 4, adapted from EPA 3052 method (10 mL HNO₃: 2 mL HF, 180°C, 40 bar), leads to higher concentrations for Cd in both CRMs studied (94 ± 5.23% in CRM-S1 and 96.92 ± 5.52% CRM-7001). The modified version of the microwave-assisted EPA method 3052 applied in the Digestion procedure 5 gave very good results for Cd determination in both CRMs soils (91.29±5.18 for CRM soil S1 and 89.57±4.8 for CRM 7001). In the case of Pb, good result was obtained only for CRM soil S1 (83.61±6.08), 71.85±3.1 being the recovery for CRM-7001.

All these 5 procedures applied on CRMs were repeated on the two polluted soils from Copsa Mică, in order to validate the best digestion procedure proven at CRMs analysis. The mean values of the total contents of heavy metal (Pb and Cd, mg·kg⁻¹·d.w.) in soil samples determined by the different digestion methods are illustrated in figure 2.

As can be seen in figure 2, the digestion procedure 4 has given the highest total content of Cd (in both soil samples) and digestion procedure 1 was the best for total content of Pb, exactly like in CRMs case.

Conclusions

The experimental results presented in this work show that all 5 microwave-assisted digestion procedures applied are generally valid for the determination of total content of Cd and Pb in polluted soils from Copșa Mică. The validation of these methods was confirmed by CRMs.

Thus, in the case of Cd determination, all 5 digestion procedures gave good recoveries (from 83.28±5.71% up to 96.92±5.52%). The digestion procedure 4 has given the highest total content of Cd (in both soil samples and CRMs), followed by the digestion procedure 5 (94±5.08%) and by the procedures 1, 2 and 3, with very close recoveries. For Pb determination, all the digestion procedures gave satisfactory recoveries in CRMs (from 63.12±8.92% up to 88.93 ± 6.92%), but the digestion procedure 1 has given the highest total content of Pb (in both soil samples and CRMs). Pb recoveries arranged in decreasing order was as follows: digestion procedure: 1 > 5 > 2 > 3 > 4.

From this comparison study it can be concluded, that in the case of Copșa Mică soils, the most appropriate digestion method for Cd is procedure 4 and procedure 1 for Pb.

Because the use of different extraction methods is time consuming and cost too much, we can suggest the use as single procedure for both metals determination (Cd and Pb), the digestion procedure 5, due to the good recoveries that is obtained for each metal determination, up to 83% for Pb and up to 91% for Cd. However, for a very accurate determination of the total content of Cd and Pb in Copșa Mică soils is recommended to use two digestion procedures (e.g. procedures 1 and 4) and calculate the average of obtained values.

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