Microwave assisted EDTA extraction—determination of pseudo total contents of distinct trace elements in solid environmental matrices

Sezin Öztan*, Rolf-Alexander Düring

Institute of Soil Science and Soil Conservation, Interdisciplinary Research Centre for Biosystems, Land Use and Nutrition (IFZ), Justus Liebig University, Heinrich-Buff-Ring 26-32, D-35392 Giessen, Germany

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ABSTRACT

Quantitative determination of metals in environmental matrices became important in the past few decades because of increasing pollutant concentrations in aquatic and terrestrial ecosystems. The extraction phase in the process of determining metals is crucial but very time-consuming. Consequently, new extraction techniques for extractable metals have been developed which probably will substitute conventional procedures in the future. The aim of this study was to improve a closed vessel microwave assisted extraction (MAE) by using EDTA as an exclusive extraction agent (MAE-EDTA) for the determination of pseudo total metal contents in solid environmental samples. For this purpose, a large set of soil and compost samples were analyzed.

MAE-EDTA was compared with both closed vessel microwave assisted aqua regia extraction (MAE-AR) and a conventional aqua regia extraction (AR) method for the determination of pseudo total Cd, Cu, Mn, and Pb contents of soil and compost samples. Certified reference materials were used for comparison of recovery rates from different extraction protocols. Metal concentrations in soil and compost extracts were determined by ICP-OES.

MAE-AR which was considered as a reference MAE method for further steps of the study, showed the same extraction yields in the determination of pseudo total metal contents of the investigated elements (As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn) in soil and compost samples as the conventional AR.

MAE-EDTA gave similar values as the reference methods in the determination of Cd, Cu, and Pb amounts in soil samples and Cd, Mn, and Pb amounts in compost samples. The recovery rates ranged between 89.0–117.1% for soil samples and 93.5–104.0% for compost samples. MAE-EDTA provides fast processing of the samples that is less than one hour, including time for cooling of the samples. Apart from significantly less processing time, minimal consumption of sample and reagent chemicals is a strategic characteristic of MAE-EDTA procedure which has advantages including accuracy and reduction of contamination. The drawback of MAE-EDTA was that the optimized conditions for the metals Cd, Cu, Mn and Pb may not be generally applicable for the other metals. Therefore, the analytical parameters available in MAE-EDTA should be further investigated for the metals of interest.

1. Introduction

Increasing concentrations of heavy metals in the environment result in continuously growing importance for elemental analysis in environmental samples [1,2]. Elevated metal loads in soil result in increased uptake by plants and thereby accumulate in the food chain. Thus any soil amendment and fertilizer such as compost, which are used as fertilizer [3], should be monitored for their elemental concentrations. Though total concentrations of metals in soil is used to characterize its base-line elemental composition (parent geological material), pseudo total metal concentration analysis allows to assess soil pollution and to ascertain heavy metal and other pollutant contents in the soil. Although different procedures have been described to determine pseudo total metal contents, the most widely adopted method is aqua regia digestion [4]. Sastre et al. [5] compared microwave-fluoric acid assisted total extraction with this conventional aqua regia extraction for Cd, Zn, Cu, and Pb in sediments, soils, sludge and plant materials and reported that both methods show similar results. Therefore, aqua regia offers a good choice for monitoring samples with low organic matter content. Conventional procedures for metal analysis such as extraction of soil samples using hot plate and concentrated strong acids are usually time-consuming and labor intensive [6]. In addition, it may result in corruption of analytes [7].

Abu-Samra et al. [8] first described microwave heating for the impetuous wet acid digestion of biological samples. From then on, the microwave digestion technique has been accepted as a rapid, effective sample preparation method for trace metal determination [9,10] to enhance elemental recoveries [11]. The closed vessel microwave assisted acid digestion system which is also useful for volatile elements has proven to be a fast and accurate method for the decomposition of several environmental and biological matrices [12]. Consequently, MAE has been applied to many fields of analytical chemistry [13–15] and is used as an effective extraction method for biological, environmental, geological, and metallic matrices.

The main advantage of MAE is the reduction of the processing time [16–18] due to direct transition of the microwave energy to the sample by absorptive polarization and concurrent heating of samples [19,20]. In conventional heating methods, a finite period of time is needed to heat the vessel before the heat is transferred to the solution [16]. Moreover, the heat is only transferred to parts of the solution that are in contact with the heat source [21]. Other advantages of MAE over traditional methods include lower reagent and sample usage, enhanced operator safety, reduced contamination, reproducible sample preparation and environmental compatibility [2,7,17,20–23].

Chelating agents contain varying numbers of functional groups that are capable of forming complexes with heavy metals [24]. EDTA (ethylenediaminetetraacetic acid) is a non-specific chelating agent and it may react with metal ions [25]. Wanekaya et al. [26] used pressure assisted chelating extraction (PACE) as a novel approach to extract metals in solid matrices and showed that EDTA is able to solubilize Pb more than water and acetic acid. The authors mentioned that the increased temperatures decrease the surface tension of the medium and matrix, allowing the medium to wet the sample matrix. Furthermore, for resulting in a clean and less hazardous metal dissolution, the usage of EDTA as an extracting medium instead of concentrated acids is attractive [27].

Our present study reports an innovative method, the use of EDTA as an exclusive extraction agent within a closed vessel MAE for the determination of pseudo total metal concentrations of selected elements in soil and compost samples.

The aim of this study is to demonstrate that closed vessel MAE-EDTA could be a good alternative to both conventional AR extraction and MAE-AR for certain metals (Cd, Cu, Mn, and Pb) for soil and compost samples. To prove this, a large set of soil and compost samples with a broad range of physical and chemical properties as well as certified reference materials were chosen to validate the method. Thereby, the applicability of MAE-AR as a reference method for MAE procedures and accuracy of MAE-EDTA was to be demonstrated.

For evaluation of the MAE techniques, ICP-OES (inductively coupled plasma-optical emission spectrometer) was chosen, due to its countenance to rapid, sensitive and simultaneous multi-element capability (over 70 elements, including all the investigated elements) [28–30].

2. Experimental

2.1. Samples

Soil samples ($n=158$), collected from the topsoil layer (0–30 cm), were taken from different locations in Hesse, Germany and from contaminated sites in Mashavera Valley, Georgia. In addition to soil samples, samples from compost ($n=27$) were also analyzed as another solid environmental matrix.

Soil samples with a broad range of physical and chemical properties were used to prove the effectiveness of both extraction

Table 1
Characteristics of soil samples ($n=158$).

Properties	Mean	Minimum	Maximum	Median
pH [CaCl$_2$]	5.92	4.08	8.00	5.55
C$_{org}$ (%)	2.66	0.11	6.13	2.34
Sand (%)	19.81	0.00	81.23	13.54
Silt (%)	44.68	0.00	80.62	45.78
Clay (%)	35.5	5.76	100.00	35.01

C$_{org}$: Organic carbon.

Table 2
Characteristics of compost samples ($n=27$).

Properties	Mean	Minimum	Maximum	Median
pH [CaCl$_2$]	7.43	4.4	8.5	7.4
O.M (%)	43.04	28.37	52.67	41.37

O.M: Organic matter.

procedures. The characteristics of soil such as soil pH (DIN ISO 10390) [31], soil carbonate content (DIN ISO 10693) [32], organic carbon by using C–N–S element analyzer (Elementar) and soil particle size distribution (DIN EN ISO 14688) [33] were determined for the samples collected. Additionally, characteristics of compost samples were tested according to the Federal Compost Quality Assurance Organization, Germany (FCQAO) [34]. The characteristics of soil and compost samples are shown in Tables 1 and 2.

2.2. Reagents and reference materials

The reagents used were all of analytical-reagent grade certified for the impurities. 69% (w/v) nitric acid (HNO$_3$) (Merck, Germany), 35% (w/v) hydrochloric acid (HCl) (Carl Roth, Germany), and solid ethylenediaminetetraacetic acid (EDTA) (Merck, Germany) were used for the extraction procedures. Distilled and deionized water, purified with a Milli-Q plus system (Millipore), was used for the experiments. Element solutions were prepared by appropriate dilution of ICP standards (Carl Roth, Germany) of the investigated elements.

The accuracy of extraction methods for soil samples were examined by analyzing two certified reference materials (CRMs), "7001" (light sandy soil) and "7004" (loam), from Analytika Co. Ltd, Prague, Czech Republic, and for compost samples by one interlaboratory test reference material (RM). To designate the amount of possible cross contamination, blank values were determined within each sample series.

2.3. ICP-OES instrumentation

Metal concentrations in soil and compost extracts were determined by an inductively coupled plasma-optical emission spectrometer (ICP-OES; Agilent 720ES, Darmstadt, Germany) with axial torch and echelle optic configuration, Charge Couple Device (CCD) detection system and full wavelength coverage from 167 nm to 785 nm (for operating parameters see Table 3).

2.4. Extraction techniques

2.4.1. Conventional aqua regia extraction procedure (AR)
The conventional AR extraction procedure was based on the International Organization for Standardization (ISO) 11466 method [35]: 3 g of soil and compost samples were extracted, respectively, with a mixture of 21 ml HCl (32%) and 7 ml HNO$_3$ (69%) in 250 ml Pyrex extraction tubes.