Development of a Method for the Microwave-assisted Digestion of Soils Using Dilute Acids and the Simultaneous Determination of 18 Trace Elements by Inductively Coupled Plasma Mass Spectrometry

Krishnan Chandrasekaran^{a,*}, Puttam Reddy Mamatha^b, and Dheram Karunasagar^a

^a National Centre for Compositional Characterization of Materials (C.C.C.M.),
Bhabha Atomic Research Centre, Department of Atomic Energy,
E.C.I.L. Post, Hyderabad-500062, Telangana, India

^b Jawaharlal Nehru Technological University Ananthapuram, College of Engineering,
Pulivendula-516 390, Kadapa, Andhra Pradesh, India

ABSTRACT

A simple two-step microwave-assisted digestion process employing dilute acids was developed for the simultaneous determination of 18 elements (Li, Be, V, Cr, Co, Ni, Cu, Zn, Ga, As, Sr, Mo, Sn, Ba, Tl, Pb, Bi, and U) in soil by inductively coupled plasma mass spectrometry. The soil sample (~0.3 g) was initially digested using a mixture of 10% (v/v) HNO₃ + 7% (v/v) HF. Subsequently, the HF was removed by evaporation, and the final solution made into a dilute HNO₃ + HCl mixture to prevent the elements from hydrolyzing. The goal was to develop a digestion method for monitoring the heavy metal content in soil samples, especially with a view to reduce the acid content and to enable the sample digests to be analyzed by inductively coupled plasma

techniques. The proposed method was validated by digesting and analyzing a certified soil reference material GBW-07409. The percentage recovery of the above trace elements varied from 86–107%. Detection limits ranging from 0.001 to 0.04 mg kg⁻¹ and relative standard deviation values lower than 10% were obtained. A standard digestion (total) procedure for soil analysis based on the USEPA 3052 method was applied and the results compared with those obtained by the developed method. Later, a sample of soil collected from Tummalapalle, Andhra Pradesh, India, where recently large uranium deposits have been identified and mining commenced, was analyzed, and the results are presented.

understanding of their effects, countries have introduced guideline values relating to the maximum levels of contaminants that may be released into or contained in the environment. Threshold levels have been prescribed particularly to soils and groundwaters as metals in soils at even slightly elevated concentration levels, whether due to natural or anthropogenic factors, can result in their entry into the food chain, thus leading to serious consequences and subsequent health problems (3, 4).

Although trace elements (Cu, Fe, Mn, Ni, and Zn) are essential plant micronutrients, elevated levels of metals in soil may lead to increased uptake by plants and affect the quality of agricultural products. Lead (Pb) is nonessential and may exhibit extreme toxicity even at low levels. For these reasons, the monitoring of trace metals in agricultural soils is essential (5, 6).

The presence of any element in high concentration in the soil could be due to both natural and/or anthropogenic factors; it is often quite difficult to discriminate among the different causes. The parent material largely influences heavy metal content in many soil types, with concentrations sometimes exceeding the critical values (7, 8). Anthropogenic sources of heavy metal content in soils result mainly due to activities such as waste disposal and combustion processes in industry and transportation; mining activities for extrac-

INTRODUCTION

Accumulation of metal contaminants in the environment is growing due to increased anthropological activities causing ecological concerns. Intense cultivation and open cast mining can lead to severe heavy metal pollution of soils. Pyrite, the most abundant sulphide found in metallic mine spoils, oxi-

dizes to sulphate, leading to formation of sulphuric acid, thus causing acidic mine drainage that may solubilize other sulphates and trace metals (1). The resulting drainage and the solubilization of heavy metals can contaminate surface and underground waters by leaching (2).

Many studies are regularly carried out with a focus on heavy metals due to their potential risks to human health, distribution in the soil, mobility and availability to the soil biota. With an increasing

*Corresponding author.
E-mail: kchandru73@rediffmail.com
Tel: 91-40-27121365
Fax: 91-40-27125463;

tion and manufacturing of metal products also result in a large amount of pollutants being released into the atmosphere and transported to the adjoining soil and waters. Long-term and intensive cultivation of agricultural land with the application of fertilizers and pesticides also results in accumulation of metals such as copper, nickel, zinc, and cadmium in the top soil (9). Soil pollution assessment becomes very complex, especially when different sources of contamination are present and their products are variably distributed. In these cases, the spatial variability of metal concentrations in soils is necessary for identifying the possible sources of contamination and to arrive at suitable strategies for soil remediation.

The low levels at which trace metals are present and are required to be determined mean that sensitive and selective methods of analysis need to be employed. Highly sensitive analytical techniques such as ICP-AES and ICP-MS often require the samples to be brought into a suitable liquid form prior to their analysis. Soils and sediments prove difficult to digest due to the presence of refractory phases and silicates. Their varied nature and differences in mineralogy from place to place make a single universal method impossible. The need to separate the anthropogenic contributions from native metal contents has led to the development of several sequential extraction schemes (10-14). The results obtained by these methods of extraction are often limited in their applicability to the determination of extractable elements using the given procedure. The lack of uniformity among these different schemes also does not allow easy comparability or validation. Therefore, the analytical results are often directly associated with the extraction scheme employed in the particular case.

Though sequential extraction procedures can provide estimates of potentially available metals and distinguish between those bound in the lattice structure of detrital minerals, the so-called residual fraction, they suffer from certain disadvantages such as limited efficiency and phase selectivity, re-adsorption during extraction, and are often labor-intensive (15). In comparison, total digestion methods enable arriving at the anthropogenic contamination levels with good accuracy. However, in these cases it is necessary to obtain pristine, uncontaminated samples of the material under consideration. Wherever such samples are at hand, total digestion yields better estimates of man-made pollution. The determination of the total content of heavy metals in soils and sediments is particularly useful to collect information on the genesis of the soil and on the level of contamination.

The total digestion methods, with conventional digestion procedures such as the use of fluxes or inorganic acids, i.e., HCl, H₃PO₄, HNO₃, HClO₄, HF, H₂SO₄ or their combinations, are labor-intensive and tedious, and often may result in contamination. The more modern methods used are microwave-assisted digestion/ leaching (16, 17) and ultrasound-assisted leaching (18). These methods greatly reduce the analysis time, their 'closed operation' can minimize or eliminate contamination, prevent loss of volatile species (i.e., Se, As, and Hg), use lower sample size and less reagent, and aid in operator safety. Additional benefits include the ability to deal with complex matrices such as soils, sludges, and sediments that do not easily lend themselves to dissolution. Laboratory microwave ovens with pressure and temperature control also tend to yield more controlled and reproducible results than the conventional methods (19). A large number of these extraction proce-

dures have often concentrated on the determination of six elements: Cd, Cr, Cu, Ni, Pb, and Zn.

Since its introduction, ICP-MS has proven to be the best multi-elemental analytical technique for the sensitive and rapid determination of trace metals. However, the presence of high acid content and organic content in the samples poses problems causing plasma instability and even extinction. The choice of sample digestion may also be the main source of systematic error, since extraction from siliceous materials by *aqua regia*, as employed in ISO 11466 (International Organization for Standardization) (20), is always liable to be incomplete (21, 22).

In view of the matrix content of many environmental samples (soils, sediments, sludges), a total digestion scheme must include the use of hydrofluoric acid (HF) to completely release the trace elements included in the aluminosilicate phase (23-27). However, the use of HF leads to long and cumbersome schemes and requires specialized sample introduction equipment when ICP techniques are used. Dilution or complexation with boric acid are often employed to overcome the problem, but it can affect the sensitivity of the method (5).

In the present work, a simple method has been developed for the microwave-assisted digestion of soil samples limiting the concentrations of acids, HNO₃ and HF, and at the same time achieving quantitative recoveries for a large number of elements: Li, Be, V, Cr, Co, Ni, Cu, Zn, Ga, As, Sr, Mo, Sn, Ba, Tl, Pb, Bi, and U. These elements are of biogeochemical importance and were determined in the digests using an ICP-MS with good sensitivity and accuracy as demonstrated by analyzing the reference material. To our knowledge, this is the first time that dilute acids have been employed for total digestion of soil

samples as opposed to selective leaching of the elements, resulting in quantitative recoveries for as many as 18 elements.

EXPERIMENTAL

Instrumentation

A VG Plasmaquad 3 inductively coupled plasma quadrupole mass spectrometer (ICP-QMS) (VG Elemental, Winsford, Cheshire, UK), situated in a class 100 laboratory, was used in this study. A Meinhard® concentric nebulizer was used for sample introduction through a water-cooled (4 °C) Scott-type double-pass spray chamber. The plasma operating conditions, such as the nebulizer flow rate, the position of the torch and RF power, and the ion lens voltages of the instrument, were optimized while continuously nebulizing a 10-µg L⁻¹ multi-element standard solution of Be, Co, Rh, In, and Bi in 5% HNO₃ in order to maximize the ¹⁰³Rh⁺ and ¹¹⁵In⁺ signals. The plasma operating conditions were selected to obtain high sensitivity across the mass range and low oxide levels. The reagents were introduced using a peristaltic pump (REGLO Digital MS-4/12, ISMATEC, Switzerland) at a flow rate of 0.7 mL min⁻¹. The operating parameters of the ICP-QMS are listed in Table I. The soil samples were digested using a closed microwave digestion system (model MARS 5, CEM, USA) with PTFE vessels.

Reagents and Solutions

All chemicals were of analytical grade, unless stated otherwise. Sub-boiled HNO₃ and HCl were prepared in-house in a class 10 clean bench, by sub-boiling in quartz stills using reagent-grade feedstock. Suprapur® grade HF (E-Merck, Darmstadt, Germany) was used in the digestion. Ultra-pure water with >18.2 MΩ-cm resistivity (Milli-Q® Element Water System, Millipore Corporation, Bedford, MA, USA)

was used for dilution of the standards, preparing the samples, and final rinsing of the acid-cleaned vessels. All sample preparations were carried out on a class 10 clean bench. A multielement stock standard solution, ICP Multielement Standard Solution VI (Merck, Germany) containing 30 elements in 6% (v/v) HNO₃ was used. Tin was added separately from a 1000-mg L⁻¹ stock standard (Merck, Germany) during the preparation of a 1 mg L⁻¹ intermediate multielement standard. Rhodium stock standard (1000 mg L⁻¹) (Merck, Germany) was diluted and used as the internal standard. Calibration standard solutions in the range 2 – 20 µg L⁻¹ were prepared in 2% (v/v) HNO₃ by diluting the multielement intermediate standard. A certified reference material (CRM) GBW 07409 Soil (National Research Centre for Certified Reference Materials, P.R. China) was used for validation of the method developed.

All laboratory ware was rinsed three times in ultrapure water after being soaked in a HNO₃ (10%, v/v) bath overnight. Samples, reagents, and standards were prepared in a

class 100 clean laboratory, containing a class 10 workbench with laminar airflow. The PTFE vessels used for microwave digestion were cleaned using 3 mL of sub-boiled HNO₃ at high power (600W) for 20 minutes at 120°C. The vessels were subsequently rinsed three times with ultrapure water.

Soil Sampling

The soil sample analyzed in this work was collected from an agricultural area in Tummalapalle village, located near the town of Pulivendula of the YSR Kadapa district, Andhra Pradesh state, India. This area contains uranium ore deposits associated with sedimentary formations, and uranium mining has been undertaken by UCIL (Uranium Corporation of India Limited), Department of Atomic Energy (DAE), India. The top 5 cm of detritus and soil was scraped off, and soil at a depth of 10 – 15 cm was collected with a corer. Subsamples from 30 locations of that area were gathered and mixed thoroughly to prepare a composite sample (10 kg). The composite sample was then powdered in a ball mill and sieved

TABLE I
Instrumental Conditions and Measurement Parameters for ICP-QMS

Model	VG Plasmaquad 3
Rf forward power	1350 W
Reflected power	2 W
Coolant gas flow rate	13.5 L min ⁻¹
Auxillary gas flow rate	0.9 L min ⁻¹
Nebulizer gas flow rate	0.8 L min ⁻¹ ; Optimized daily
Nebulizer	Meinhard® concentric
Spray chamber	Double pass Scott-type, water-cooled at 4 °C
Ni Sampler cone orifice	1.0 mm dia
Ni Skimmer cone orifice	0.7 mm dia
Dwell time	10 ms
Data acquisition mode	Peak Jump
Points per peak	3
Sample flow rate	0.7 mL min ⁻¹
Element	⁷ Li, ⁹ Be, ⁵¹ V, ⁵² Cr, ⁵⁹ Co, ⁶⁰ Ni, ⁶³ Cu, ⁶⁶ Zn, ⁷¹ Ga, ⁷⁵ As, ⁸⁶ Sr, ⁹⁸ Mo, ¹¹⁵ In, ¹²⁰ Sn, ¹³⁷ Ba, ²⁰⁵ Tl, ²⁰⁸ Pb, ²³⁸ U

through a 200-mesh sieve to get a fine powder of < 75 μm size. The sieved samples were stored in dry polypropylene bottles.

Microwave-assisted Digestion

A sample (~0.3 g) of the soil was weighed accurately into a well-cleaned PTFE digestion vessel, in triplicate. A mixture of 10% (v/v) HNO_3 + 7% (v/v) HF (10 mL) was added and left standing at room temperature for 15 minutes for pre-digestion. Subsequently, the sample was introduced into the microwave digestion system and the program used is listed in Table II. After cooling, the digest was transferred into a 15-mL centrifuge vial and made up to a known volume and centrifuged at 5000 rpm. A suitable aliquot of the solution was taken into an acid-cleaned 7-mL PFA vial and evaporated over an IR lamp in a laminar flow clean bench to incipient dryness to remove excess HF. Care was taken to avoid heating beyond 90 $^\circ\text{C}$ to prevent any loss of solution by sputtering and/or splashing. When a few drops (100 - 200 μL) of the solution were left, with traces of white residue at the bottom of the vial, 600 μL of HNO_3 , 200 μL of HCl, and 1 mL of water were added and warmed for a few minutes until the residue dissolved completely. The solution was made up to a known volume with ultra-pure water and stored at 4 $^\circ\text{C}$ until further analysis. A process blank was prepared simultaneously as above without the sample.

USEPA 3052 Microwave Digestion Procedure

US EPA 3052 is a standard method, applicable to the microwave-assisted acid digestion of siliceous matrices, organic matrices, and other complex matrices aimed at total decomposition (28). This method was employed for validation of the proposed new method. About 0.3 g of sample was

digested using 9 mL of sub-boiled HNO_3 and 4 mL of concentrated HF; and the microwave program is listed in Table II.

TABLE II
Microwave Digestion Program

Power (W)	Ramp (s)	Temp ($^\circ\text{C}$)	Hold (min)
600	5	100	10
600	5	150	10
600	5	200	10
600	-	0	2
600	2	220	5

ICP-MS Measurements

Amounts of 1 mL and 0.2 mL of the sample digests were pipetted into two well-cleaned 15-mL polypropylene (PP) centrifuge vials. Then, 0.1 mL of 1 mg L^{-1} Rh was added as the internal standard to correct for any instrumental drift during the analysis. The solutions were then diluted to 10 mL with 2% (v/v) HNO_3 , resulting in 10 and 50 times dilution, respectively. Two different dilutions were necessary to cover all of the 18 elements, as some of the elements are present at higher levels. The process blank solutions were diluted accordingly. For each solution, the entire mass range was scanned and data was acquired three times; the mean value of the signal was used for quantification. The above solutions were quantified by external calibration using multielement standards prepared in 2% (v/v) HNO_3 containing 10 $\mu\text{g L}^{-1}$ Rh as the internal standard. A multielement standard of known concentrations of the analytes was prepared separately as a quality control sample and after every three samples it was checked for instrument performance. The signal intensities obtained for the respective blanks were subtracted from the sample and the standard.

RESULTS AND DISCUSSION

Various standard digestion methods (20, 28-30) have been reported in the literature for the analysis of soil and sediment samples for their metallic constituents. Different combinations of acids (HNO_3 , HF, HCl, etc.) have been suggested for the digestion or extraction of the trace elements in the soil. All of these methods are based on strong acid digestions. In USEPA Method 3050B (30), the soil/sediment is digested with repeated additions of nitric acid and hydrogen peroxide, followed by addition of hydrochloric acid, while in the ISO 11466 method (20), the sample is pre-digested overnight in an HCl - HNO_3 mixture (*aqua regia*) and then heated, followed by dilution with HNO_3 . These procedures, however, are not total digestion techniques as the elements associated with silicates remain undissolved. The use of HF becomes unavoidable to extract such metal ions. Similarly, the total digestion method of US EPA 3052 (29) employed herein for validation purposes also requires a mixture of concentrated HNO_3 and HF.

However, the use of concentrated acids, especially HF, complicates the subsequent analysis where ICP techniques (AES/OES or MS), two of the most sensitive and rapid analytical techniques, are employed for the analysis of metallic constituents. In addition, the use of large volumes of concentrated acids can also lead to higher process blanks, affecting the sensitivities achieved. Unlike these methods, the method proposed herein achieves almost complete digestion (with very little traces of silica) using a mixture of dilute HNO_3 and HF, employing a closed microwave digestion technique to prevent any possible loss of analytes, and is especially suitable for ICP analysis.

Method Validation

The Chinese certified reference material GBW-07409 Soil was analyzed by the developed method, followed by soil samples from Tummalapalle, Andhra Pradesh, India. The concentrations of 18 trace elements were determined in both samples and are reported in Tables III and IV. The standard US EPA 3052 method was used for comparison purposes with the proposed digestion procedure. As may be seen from these results, there is excellent agreement of the results. Applying the Student's *t*-test and comparing the certified values of GBW-07409 Soil with the mean value obtained by the proposed method showed good agreement at the 95% confidence level. In addition, by applying the paired-comparison *t*-test with multiple samples (18 elements) showed that the results of the two independent methods for both soil samples (GBW-07409 and soil from Tummalapalle) did not differ significantly at the 95% confidence level. The *p*-values obtained for GBW-07409 Soil and Tummalapalle soil were 0.25 and 0.50, respectively. As shown in Tables III, the recoveries obtained by the developed method range from 86% to 104%, which is quite similar to those obtained by the US EPA 3052 method for the GBW 07409 reference sample.

Effect of HF Concentration

An acid mixture of 10 mL containing different concentrations of HNO₃ and HF was used during optimization, the use of HF being essential to completely break the complex silicate matrix to extract the trace elements. The closed microwave digestion program used is given in Table II. Initially, the digestion was performed using 10% (v/v) HNO₃ without adding HF. Then the effect of increasing the concentration of HF to 2% (v/v), 5% (v/v), 7% (v/v), and 10% (v/v) was investigated. The use of

TABLE III
Concentration Values Obtained for GBW-07409 (in mg kg⁻¹)

Elements	Certified Concentration	US EPA 3052 Conc. $\pm$ s.d. ^a	(%) Recovery	Present Method Conc. $\pm$ s.d. ^a	(%) Recovery
Li	14.3	12.2 $\pm$ 0.6	85	13.1 $\pm$ 0.8	92
Be	2.1	2.2 $\pm$ 0.1	104	2.0 $\pm$ 0.2	96
V	34.7	37.1 $\pm$ 0.9	107	35.1 $\pm$ 0.7	101
Cr	26.4	27.1 $\pm$ 1.1	103	24.4 $\pm$ 1.0	92
Co	4.9	5.1 $\pm$ 0.3	104	5.0 $\pm$ 0.2	102
Ni	9.3	9.8 $\pm$ 0.3	105	9.7 $\pm$ 0.2	104
Cu	4.9	5.2 $\pm$ 0.4	106	5.0 $\pm$ 0.3	103
Zn	34.2	36.0 $\pm$ 1.1	105	33.3 $\pm$ 0.5	97
Ga	14.6	14.8 $\pm$ 0.2	102	15.2 $\pm$ 0.2	104
As	2.9	3.1 $\pm$ 0.2	107	3.0 $\pm$ 0.1	103
Sr	270	246 $\pm$ 20	91	247 $\pm$ 14	91
Mo	0.43	0.41 $\pm$ 0.02	95	0.38 $\pm$ 0.02	88
Sn	1.4	1.5 $\pm$ 0.1	107	1.3 $\pm$ 0.1	93
Ba	693	681 $\pm$ 30	98	638 $\pm$ 25	92
Tl	0.58	0.6 $\pm$ 0.1	103	0.5 $\pm$ 0.1	94
Pb	16.3	15.3 $\pm$ 0.4	94	15.8 $\pm$ 0.3	97
Bi	0.1	0.1 $\pm$ 0.02	100	0.1 $\pm$ 0.03	89
U	1.6	1.5 $\pm$ 0.1	94	1.4 $\pm$ 0.1	86

^a s.d. = standard deviation of n = 3 replicates.

TABLE IV
Concentration Values Obtained for Tummalapalle Soil (in mg kg⁻¹)

Elements	US EPA 3052 Conc. $\pm$ s.d. ^a	Present Method Conc. $\pm$ s.d. ^a	Relative (%) Difference
Li	23.6 $\pm$ 1.0	25.1 $\pm$ 0.4	6.4
Be	1.7 $\pm$ 0.1	1.8 $\pm$ 0.1	5.9
V	131 $\pm$ 4	137 $\pm$ 3.0	4.6
Cr	92.5 $\pm$ 2.5	93.8 $\pm$ 2.0	1.4
Co	22.5 $\pm$ 1.0	23.8 $\pm$ 0.5	5.8
Ni	60.7 $\pm$ 2.1	63.4 $\pm$ 1.0	4.4
Cu	68.6 $\pm$ 2.7	72.5 $\pm$ 1.3	5.7
Zn	45.1 $\pm$ 3.0	42.1 $\pm$ 1.2	6.6
Ga	13.1 $\pm$ 1.0	13.5 $\pm$ 0.3	3.0
As	17.8 $\pm$ 1.4	18.0 $\pm$ 1.0	1.1
Sr	52.3 $\pm$ 2.1	53.2 $\pm$ 1.5	1.7
Mo	2.4 $\pm$ 0.2	2.3 $\pm$ 0.1	4.2
Sn	1.6 $\pm$ 0.1	1.5 $\pm$ 0.1	6.2
Ba	692 $\pm$ 58	621 $\pm$ 43	10.3
Tl	0.5 $\pm$ 0.1	0.4 $\pm$ 0.1	20.0
Pb	12.1 $\pm$ 1.2	10.9 $\pm$ 0.5	9.9
Bi	0.4 $\pm$ 0.1	0.4 $\pm$ 0.1	5.1
U	4.5 $\pm$ 0.1	4.2 $\pm$ 0.1	6.7

^a s.d. = standard deviation of n = 3 replicates.

10% (v/v) HNO₃ + 7% (v/v) HF acid mixture gave quantitative recoveries (86–107%) for the highest number of elements (18 elements) as listed in Tables III and IV. Increasing the concentration of HF beyond 7% did not show any further improvement in recoveries. The use of 10 mL of a mixture of 10% (v/v) HNO₃ + 7% (v/v) HF for approximately 0.3 g sample resulted in almost complete digestion, with minor traces of silica, which did not affect the recovery of the trace elements. This was apparently based on the fact that addition of further HF did not yield any improvement in the recoveries.

Removal of HF for Analysis by ICP-MS

The digested solution containing close to 10% (v/v) HNO₃ and 7% (v/v) HF could not be passed directly into the ICP-MS for analysis as the high concentration of HF is detrimental to the glassware used in the sample introduction system. But any dilution of the sample could result in the level of the analytes falling below the detection limits. Thus, for both digestion methods, an aliquot of the digested solution was evaporated over an IR lamp to incipient dryness until white residue was seen at the bottom of the container. The residue was treated with 600 µL of HNO₃, 200 µL of HCl, and 1 mL of ultrapure water and warmed for a few minutes over the IR lamp, cooled, and made up to a known volume with ultrapure water to get a clear solution. HCl was added to stabilize elements such as Sn, Ba, etc. To check for any loss of analyte by volatilization while removing the HF, a known amount of multielement standard was spiked at two different concentration levels (0.5 and 1.0 µg absolute) to the digested solution, before evaporating over the IR lamp. The % recovery of all of the elements reported was between 90 to 100%. Even for

volatile elements like arsenic, the % recovery was quantitative.

Analytical Characteristics

The analytical characteristics of the target elements were studied using the optimized microwave digestion procedure with dilute acids. The limits of detection (LOD) calculated based on three times the standard deviation of the process blank (n = 6) for both methods are listed in Table V. The detection limits obtained, as can be seen, by the present method showed an improvement by an order of magnitude for elements Cr, Cu, Zn, As, Sr, and U when compared to the US EPA 3052 method, possibly due to better signal stability obtained by using dilute acids. For the rest of the elements, the detection limits were similar.

The reproducibility of the proposed method was obtained by digesting the CRM GBW- 07409 Soil in duplicate on 6 different days and then analyzing it. The RSD values obtained for the 18 elements were lower than 10%, except for Tl and Bi, which were found to be present at very low concentrations in the analyzed soil samples. The process blank values calculated with respect to sample weight for both digestion methods are listed in Table VI. Although both digestion methods were performed under closed microwave conditions, the process blank values, as shown in Table VI, are higher for the US EPA 3052 method compared to the proposed method for most of the elements. Thus, the advantages of the proposed method are low process blank values, determination of 18 elements in a single analysis, and the ability to obtain exhaustive chemical information in the shortest time possible. Most of the methods reported in the literature have often focused on determining fewer elements, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn in soil using

TABLE V
Limit of Detection (n = 6)

Element	US EPA 3052 (mg kg ⁻¹)	Present Method (mg kg ⁻¹)
Li	0.003	0.003
Be	0.003	0.004
V	0.002	0.001
Cr	0.03	0.008
Co	0.001	0.003
Ni	0.015	0.015
Cu	0.2	0.004
Zn	0.1	0.02
Ga	0.006	0.003
As	0.2	0.04
Sr	0.06	0.007
Mo	0.004	0.001
Sn	0.02	0.008
Ba	0.008	0.004
Tl	0.003	0.001
Pb	0.036	0.007
Bi	0.013	0.003
U	0.030	0.003

TABLE VI
Process Blank Values (n = 6)

Element	US EPA 3052 (mg kg ⁻¹)	Present Method (mg kg ⁻¹)
Li	0.01	0.01
Be	0.03	0.002
V	0.04	0.02
Cr	0.32	0.18
Co	0.01	0.004
Ni	0.4	0.2
Cu	3.7	0.3
Zn	1.6	0.3
Ga	0.01	0.01
As	2.30	0.15
Sr	0.03	0.02
Mo	0.01	0.01
Sn	0.2	0.1
Ba	0.15	0.04
Tl	0.004	0.003
Pb	0.3	0.06
Bi	0.06	0.01
U	0.008	0.007

concentrated acids. The concentrations of the trace elements reported for the soil samples in Tables III and IV are corrected for moisture content of the samples.

Analysis of Real Soil Sample

The Uranium Corporation of India Limited (UCIL) established a uranium mining and milling facility at Tummalapalle, YSR Kadapa district, Andhra Pradesh state, India, to meet the energy security for the nation. To ensure that the uranium mining activity does not significantly influence the existing environmental quality in and around the villages during extraction, it is essential to establish a preliminary survey of the elemental contents of soil and other parameters in and around the site to generate extensive baseline data. A finely powdered soil sample was digested by the developed method and compared with the standard US EPA 3052 method for its trace elemental content. The results in Table IV show that the two methods are in good agreement. The concentration of uranium and other elements are at slightly elevated levels. The use of fertilizers and pesticides over a long period of time might have led to the accumulation of these trace elements in the soil collected from agricultural land. Our laboratory is in the process of making a soil reference material. The results show that this soil sample could be a suitable candidate for preparing a soil reference material with trace elements at high levels.

CONCLUSION

An environmentally friendly method for the total digestion of the soil samples, followed by determination of 18 elements (Li, Be, V, Cr, Co, Ni, Cu, Zn, Ga, As, Sr, Mo, Sn, Ba, Tl, Pb, Bi, and U) has been reported. The total digestion of soil was achieved using dilute acids [10% (v/v) HNO₃ + 7% (v/v) HF]

unlike many total digestion methods that often employ mixtures of concentrated acids using closed microwave digestion. The present method allows a large number of metal constituents to be determined quantitatively, requires shorter digestion times, and offers good recoveries for the volatile elements. In addition, the use of dilute acids has resulted in low process blank values with better detection limits (0.001 to 0.04 mg kg⁻¹). The high reproducibility of the method shows that it can be routinely used for the determination trace elements in soil.

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