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Determination of total content of some microelements in soil using two digestion methods

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Abstract

Aqua regia and tri-acid digestion methods were applied for the analysis of some soil microelements. The total number of 243 soil samples was digested using the two different methods and total Iron, Manganese, Zinc, and Copper were measured in extracted solutions using atomic absorption spectrophotometer (AAS). The obtained results showed a strong correlation between two digestion methods of microelements, $r=0.95$, 0.81 , 0.85 and 0.84 for Iron, Manganese, Zinc, and Copper, respectively. The two methods of digestion were able to extract the total content of microelements with similar efficiency. The aqua regia method was found to be less chemical consuming, less harmful to the environment, time and cost-efficient than the tri-acid digestion method. Thus, the aqua regia method of digestion is strongly recommended for analysis of the total content of microelements in soils.

Keywords: Aqua regia digestion, tri-acid digestion, microelements, AAS

Introduction

This work aimed to apply two different digestion methods (aqua regia and tri-acids) for determination of the total content of some microelements (Iron, Manganese, Zinc, and Copper) in soil. Microelements estimation in soils and sediments at levels of ppm or ppb is particularly useful to collect information on the genesis of the soil and the level of contamination [1]. For this purpose, the speed and efficiency of instrumentation for reliable determination of trace elements in geological and environmental samples have improved dramatically over the last decades. Atomic absorption spectrometry (AAS) and inductively coupled plasma-optical emission and mass spectrometry (ICP-OES and ICP-MS) are among the most common spectroscopic methods used for the determination of microelements in soils. The drawback of these techniques is that the solid sample is required to be digested and brought into solution-phase before the determination of the metal content [2]. Therefore, sample preparation is an important step in the analysis of soils because of the refractory nature of these materials [3]. Sample preparation methods are still the major factor contributing to the uncertainty in the analytical results [4]. Conventional digestion procedures, such as wet digestion and dry ashing, are often the most time-consuming stage of the analysis. These methods are labor-intensive and tedious, and often have a high contamination potential [5]. A large number of different acid mixtures have been used for digestion. Some methods use HNO_3/HF ; others use $\text{HClO}_4/\text{HNO}_3$; $\text{HF}/\text{HNO}_3/\text{HCl}$, HNO_3/HCl , and $\text{HNO}_3/\text{H}_2\text{SO}_4$. In most cases, complete digestion of the sample is required to achieve reproducible and accurate results [6]. According to the completeness of extraction, the analytical methods for determination of trace elements values in soils or sediments can be subdivided into two main groups *viz*, real total contents (totals) and partial contents [7]. Aqua regia digestion is widely used for the determination of the harmful chemical elements in the soil aiming to solve environmental pollution [8]. It can be termed as 'Pseudo total' [9]. Some researchers point out that in topsoil, where residual silicates do not display high metal concentrations, the values obtained by aqua regia digestion are representative of the total metal concentration [10]. On the other hand, geochemical exploration or mapping cannot do without the determination of real total contents [11]. According to Reimann *et al.* [12], "Geologists would prefer to use analytical results from the "total" dissolution of microelements by tri-acid ($\text{HF}+\text{HClO}_4+\text{H}_2\text{SO}_4$) digestion method for estimation of total element concentrations".

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Materials and methods

Soil sampling and pretreatment

A total of 243 soil samples were collected from the three different agricultural areas in Karnataka and Andhra Pradesh, India. Topsoil samples were collected 0–20 cm depth using a

soil auger. The samples were air-dried, grounded with porcelain mortar and pestle, passed through 0.50 mm sieve and kept in clean polythene containers for further analysis. Figure (1) shows the soil sampling locations.

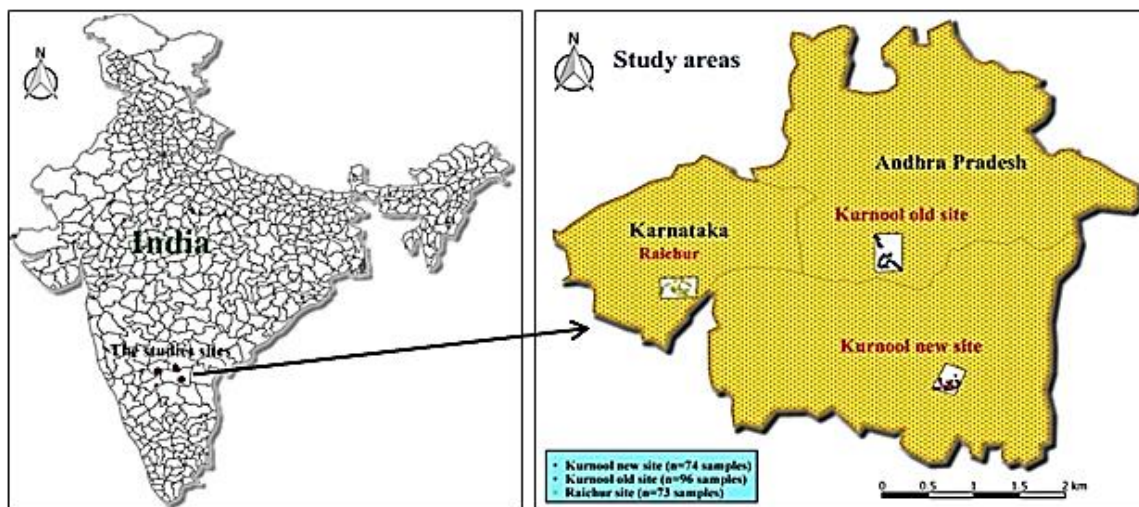


Fig 1: The soil sampling locations

Equipment

An electronic analytical balance was used for weighing the soil samples. An electronic hot plate with a controlled fume hood was used to digest the soil samples. Flame atomic absorption spectrophotometer equipped with deuterium lamp background correction and hollow cathode lamps was used for the analysis of the total content of the microelements (Iron, Manganese, Zinc, and Copper).

Chemicals and reagents

Hydrochloric acid (HCl 35–38%), Nitric acid (HNO₃ 65–68%), Sulfuric acid (H₂SO₄ 95–79%), Hydrofluoric acid (HF 48%) and Perchloric acid (HClO₄ 70 to 72%) of analytical grade AG (Merck-Germany) were used for samples digestion. The 1000 ppm stock standard solutions of the microelements (Iron, Manganese, Zinc, and Copper) were used to prepare the calibration standard curve. Double distilled water was used throughout the study. The glassware, Teflon beakers and polyethylene containers used for analysis were washed with tap water, then soaked overnight in 10% (v/v) HNO₃ solution and rinsed several times with double distilled water to eliminate absorbance due to detergent.

Aqua regia digestion

Since the determination of total microelement content in soil using hydrofluoric acid (HF) is time-consuming and cumbersome, nowadays focus is on pseudo total (aqua regia extractable) content to assess the extent of metal pollution in the soil. It is assumed in devising aqua regia extraction procedure that fraction of microelement, which is not extractable with aqua regia would not have much adverse impact on soil flora and fauna as well as plants. This extraction technique (aqua regia extractable) can easily be adopted for routine estimation of total microelements in soils due to its rapidity [13].

Procedure

Two grams of soil sample were taken in a 150ml conical flask, added 18.75 ml HCl followed by slow addition of 6.25ml HNO₃ with the help of a 25ml measuring cylinder

through the inner wall of the conical flask. Placed a funnel on the flask and kept for 6–8 hours or overnight for pre-digestion. Prepared a blank without soil. Heated the content on hot plate to the boiling point until the content is reduced to 2–3ml. Added about 50ml of DDW and mixed the content thoroughly. Filtered the content through Whatman No.42 filter paper in a 100ml volumetric flask with 2 to 3 times of washing the conical flask with DDW. Made up the volume to the mark. Stored the extracts for the estimation of total microelements by atomic absorption spectrophotometer [14].

Tri-acid digestion

Procedure

Placed 0.10g sample of finely ground soil in 50ml Teflon cups. The soil was wetted with a few drops of H₂SO₄ and added 5ml of HF and 0.50ml of HClO₄. With organic soils, added 3ml of HNO₃ and 1ml of HClO₄ to the Teflon cup, heated a soil-acid mixture on an electronic hot plate until fumes of HClO₄ appear. Cooled the Teflon cups and added 5ml of HF. Placed the cups in the hot plate, and covered about nine-tenths of the cup to with a Teflon lid. Heated the contents between 100 and 200°C, and evaporated the contents to dryness. Cooled the cup, and added 2ml of DDW and a few drops of HClO₄. Replaced the cups in the hot plate again, and evaporated the content to dryness. If organic matter stains are still present on the sides of the lid of the Teflon cup, added a few drops of HNO₃ and reheated the content till organic matter removal. If the sample does not dissolve completely, evaporated the solution to dryness and repeated the procedure, starting with 1drop of H₂SO₄, 5ml of HF, and 0.5ml of HClO₄. When the residue completely dissolved in HCl, transferred the sample to a 50ml volumetric flask, and diluted the contents to make up the volume. Stored the solutions for analysis using the atomic absorption spectrophotometer [15].

The elemental analysis

After digestion, the extracts were subjected to elemental analysis in an atomic absorption spectrometer (SPECTRUM-SP-AA4000) to determine the concentrations of Iron, Manganese, Zinc, and Copper in the extracted samples.

Statistical analysis

All applied statistical calculations and data plotting purposes were done using MS-excel software. For comparing efficiency between the two applied methods, the correlation test was applied. The correlation coefficient r could compare the two methods of digestion for each analyzed microelement individually. Equation (1) showed the applied formula for calculating the correlation. Equation (2) showed the calculation of the standard deviation of the data obtained from each applied method. The obtained data were plotted to interpret the results and find the correlation coefficient r among the two digestion methods for each microelement (Figure.2).

$$r = \frac{1}{n-1} \sum_{i=1}^n \left(\frac{x_i - \bar{x}}{s_x} \right) \left(\frac{y_i - \bar{y}}{s_y} \right) \quad (1)$$

$$s = \sqrt{\frac{\sum (x - \bar{x})^2}{n-1}} \quad (2)$$

Where (n) is a number of analyzed samples; S_x and S_y are the standard deviations of data obtained from the two methods of digestion for each analyzed total elements individually; x_i and y_i are the values or observations for the two applied methods; \bar{x} and \bar{y} are the mean values of the data sets from the two digestion methods for each analyzed microelement.

Regression line and R^2 were calculated and the data were plotted to present the relation between the studied methods. Equations (3, 4 and 5) showed the calculation of regression line \hat{Y} and prediction equations development for each element individually.

$$\hat{Y} = b_0 + b_1 x \quad (3)$$

$$b_1 = \frac{n(\sum xy) - (\sum x)(\sum y)}{n(\sum x^2) - (\sum x)^2} \quad (4)$$

$$b_0 = \frac{(\sum y)(\sum x^2) - (\sum x)(\sum xy)}{n(\sum x^2) - (\sum x)^2} \quad (5)$$

Results and discussion

The 243 soil samples were digested using two different methods and the total content of some microelements (Iron, Manganese, Zinc, and Copper) were determined. The minimum, maximum, mean and standard deviation (SD) of each obtained data set were calculated. The correlation coefficient r of the two data sets of the two applied digestion methods (aqua regia and tri-acid digestion) methods was also calculated. The obtained results from the two applied digestion methods were shown in Table (1). Figure (2) showed the means comparison charts of total elements extracted by the two different methods.

Table 1: The statistical analysis of the total microelements obtained data.

Total content	Aqua regia				Tri-acid				r	R^2
	Min.	Max.	Mean	SD	Min.	Max.	Mean	SD		
Total Iron (%)	0.03	12.18	4.06	2.24	0.14	14.26	4.57	2.44	0.95	0.90
Total Manganese (%)	0.01	1.63	0.41	0.21	0.11	2.00	0.49	0.25	0.81	0.66
Total Zinc (mg/kg)	5.00	44.25	20.88	5.88	4.50	55.00	23.94	7.29	0.85	0.72
Total Copper (mg/kg)	3.00	83.25	19.09	7.96	2.00	114.00	22.02	9.08	0.84	0.71

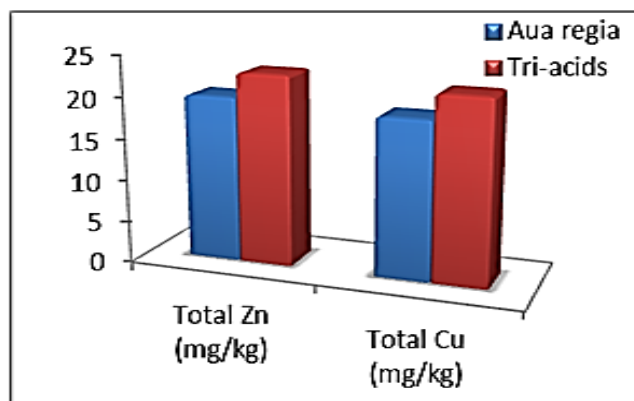
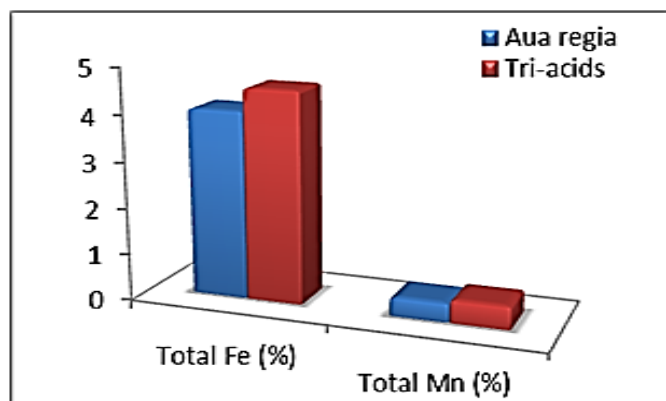


Fig 2: The comparison of total microelements extracted by different methods.

For the aqua regia and tri-acid digestion methods, the total Iron ranged between 0.03-12.18 and 0.14-14.26 with an average of 4.06 and 4.57%, respectively. The total Manganese values were varied between 0.01-1.63 and 0.11-2.00% with an average of 0.41 and 0.49% for aqua regia and tri-acid digestion methods, respectively. The total content of Zinc ranged between 5.0 and 44.25 mg/kg for the aqua regia method and from 4.50 to 55.0 mg/kg for the tri-acid method of digestion. The values of total Copper in soil varied from 3.00 to 83.25 mg/kg soil, for aqua regia and ranged from 2.00 to 22.02 mg/kg soil, for the tri-acid digestion method. From the obtained results, it is obvious that the mean data of total microelements (Iron, Manganese, Zinc, and Copper) extracted from the soils with aqua regia and tri-acid digestion method

were comparable to each other. The standard deviation of the obtained values showed that total Iron and Manganese had a similar trend; while it was slightly different for total Zinc and Copper. Correlation values for the two digestion methods (Figure 3) showed a strong correlation between the digestion methods ($r > 0.80$). The r values were 0.95, 0.81, 0.85 and 0.84 for Iron, Manganese, Zinc, and Copper, respectively. From the obtained results, it is evident that the two digestion methods were able to extract the total content of microelements with similar efficiency. This is also evident from the regression equations (Figure 3) in which R^2 values were 0.90, 0.66, 0.72 and 0.71 for Iron, Manganese, Zinc, and Copper, respectively. Thus, from this study, the two methods of digestion were found to show a similar efficiency in soil

total microelements extraction. These results were in agreement with those obtained by Santoro *et al.*,^[16]. They mentioned that there is a small difference (less than 10%) between the ability of the two applied methods for releasing the total content of microelements from the soil samples. According to Sastre *et al.*^[2], aqua regia contents of total microelements in soil samples do not differ much from real total contents obtained by digestion with tri-acid digestion method.

As aqua regia digestion method is having more advantages over the tri-acid digestion method such as (1) less chemicals consuming which only two acids (HCl and HNO₃) used while, five different acids (H₂SO₄, HNO₃, HF, HClO₄ and HCl) are required for tri-acid digestion method; (2) the time which is consumed for digesting soil samples in case of aqua regia

method is less compared to tri-acid digestion method; (3) in the absence of fume hood in soil laboratory, the aqua regia method is more suitable because it produces fewer fumes than tri acid digestion which will cause less environmental hazardous pollution when digested in open place; (4) the extract solution obtained from aqua regia digestion is less harmful to the sprayer part either in AAS or ICP compared the acids used in the tri acid digestion method especially HF and HClO₄ which may damage the silicate parts of these instruments even if it is used in low concentration; and (5) the aqua regia digestion method is more cost effective compared to the tri acid digestion method because it is less chemicals consuming. Thus, from this study, the aqua regia method of digestion can be recommended to digest and prepare soil samples for total microelements analysis.

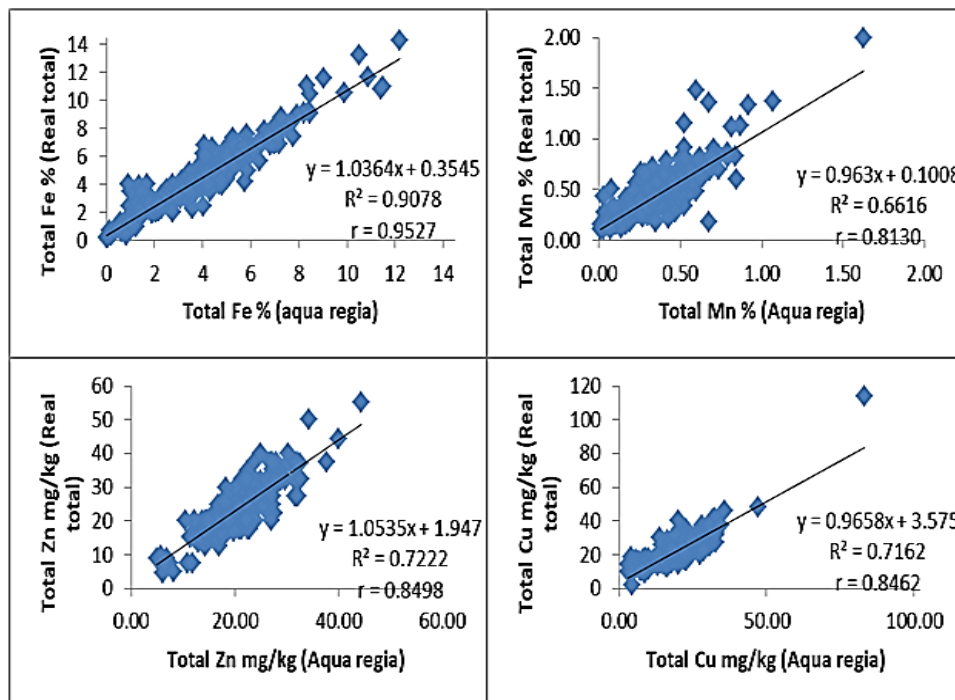


Fig 3: The correlation and regression of the aqua regia and tri-digestion methods

Conclusion

The two digestion methods (aqua regia and tri-acids) were compared for their ability to extract the total content of microelements in the solution phase. Similar efficiency for extraction of Iron, Manganese, Zinc, and Copper from soil was recorded for the two digestion methods. The aqua regia digestion was found to be faster, less harmful to the environment, time and cost-effective than the tri-acid digestion method. Thus, the aqua regia digestion method is recommended for the digestion of soil samples for estimation of the total content of microelements in soils.

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