

Multinutrient Extraction – Need of the Hour – A Review

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ABSTRACT

A Multi nutrient extractant is a standardized reagent which is capable of extracting several elements or ions simultaneously to facilitate quick estimation of soil macro and micronutrients saving time, labour and resources. The procedure for extraction should be rapid, consistent, less expensive, reliable and considerate of the soil physico-chemical properties. Progressive research on developing such an extractant and an extracting procedure has resulted in various extractants such as Morgan reagents, Mehlich reagents, Diethylene Triamine Pentaacetic Acid (DTPA), ammonium bicarbonate- DTPA(AB-DTPA) and various other formulations. This article presents a comprehensive review of all the multinutrient extractants developed so far and their advantages and limitations in the extraction of soil macro and micronutrients, their efficiency in the extraction of nutrients and correlation with standard extraction procedures. Also, the potential utility of multi nutrient analysers such as Inductively Coupled Plasma – Optical Emission Spectrometry and Atomic Absorption Spectrometers can be achieved by employing appropriate multi nutrient extractants in the estimation of soil nutrients which could establish significant relationship between estimated nutrients and crop response. The selection of an appropriate multi nutrient extractant and the standard extracting procedure is commendable and is the need of the hour to support the fertilization schedule for crop cultivation and sustainable maintenance of soil health which has direct implication on food and nutrition security and ecological sustainability.

Key words: Multinutrient extractant, Morgan reagent, Mehlich reagent, Correlation analysis, Available soil nutrients.

Introduction

The drive for targeting higher agricultural production needs a balanced use of nutrients which otherwise create problems of soil fertility exhaustion and nutrient imbalances of major, secondary and micronutrients. Crop yields may be limited by nutrient deficiency caused by the low natural fertility of some soils, considerable nutrient removal by harvests and excessive application of fertilizers and substances for correction of soil acidity, causing an imbalance of nutrients in the soil and also insolubility of micronutrients in the soil. The prevailing deficiencies of micronutrients pose a serious threat to crop productivity and sustainability of soils. There-

fore, soil diagnosis is an important activity carried out by extension services of the Government, Agricultural Universities and private farms in order to get the nutrient status of the soil. A rapid diagnosis method of soil nutrients is required to save time and labour, because many soil samples gather at the same time particularly during sowing season (Uwasawa, 1994).

The existing analytical methods for estimation of soil available nutrients are quite effective and accurate but involve separate extractants and procedures for the extraction of various nutrients. Therefore, these procedures are more time consuming, laborious, cumbersome, and costly because of more use of chemicals, glassware, and energy. In order to over-

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come these issues, multi-nutrient extractants offer a suitable alternative, as more than one nutrient can be extracted in one go (Bibiso *et al.*, 2015). Thus, a method of extracting multi nutrients simultaneously for the diagnosis of available soil nutrients should be developed (Nakatsuka *et al.*, 1988).

Morgan's reagent

The first universal soil extracting reagent, 0.73M sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$) solution buffered at pH 4.8. was developed by Morgan (Morgan, 1941). The Morgan extractant procedure was described in the Connecticut Experiment Station Bulletin 450 In 1941, which was followed by Bulletin 541 in 1950 where, the analytical procedures and interpretative data for the determination of 15 elements and ions were described. The Morgan extraction reagent was widely used in the 1950s and early 1960s, but it is of little use today. Nutrients determined by this reagent include P, K, Ca, Mg, Cu, Fe, Mn, Zn, NO_3^- , NH_4^+ , SO_4^{2-} , Al, As, Hg, Pb. The pH 4.8 simulates the carbon dioxide saturated solution adjacent to the root hairs and acts as a mild solvent for iron and aluminium phosphates and other minerals essential in plant nutrition. The sodium acetate is effective in replacing important soil cations and anions into the extract solution which could be measured. The use of sodium acetate and acetic acid permitted the determination of all important soil nutrients except sodium.

Wolf reagent (Modified Morgan's reagent)

Wolf modified Morgan's reagent for use with acid to neutral pH soils irrespective of texture as the soil aliquot measurement is by volume (Wolf, 1982). The extraction reagent is a mixture of 0.073M sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$), 0.52N acetic acid (CH_3COOH) and 0.001M diethylenetriamine pentaacetic acid (DTPA) buffered at pH 4.8. The extraction reagent is best suited for the assay of well fertilized soils and most effective for monitoring their fertility level.

Mehlich no. 1 (M 1) reagent

Mehlich No. 1 extractant was introduced for the determination of P, K, Ca, Mg, Na, Mn and Zn in acid sandy soils (Mehlich, 1953). The extraction reagent is a mixture of 0.05N HCl in 0.025N H_2SO_4 . The acid used in the reagent extracts elements from acid soluble fraction as well as water soluble and exchangeable fraction from soil. However, Double Acid is not recommended for calcareous soils or on acid soils containing recently applied rock phos-

phate as it extracts P in considerable excess of that obtained with Bray 1 and Olsen.

Mehlich no. 2 (M 2) reagent

In 1978, Mehlich modified M 1 reagent for simultaneous extraction of several plant nutrients. The new extractant is composed of 0.2N NH_4Cl , 0.2N HOAc, 0.015N NH_4F and 0.012N HCl at pH 2.5. In acid soils in the absence of phosphate rock improved extraction efficiency and correlation with Bray 1 were obtained by increasing the soil: extractant ratio of the DA method from 1:5 to 1:10 and by adding HF or NH_4F to the reagent. Recent observations by Mehlich showed that precipitation of CaF_2 was not restricted to calcareous soils, but may occur in neutral and acid soils. It was also shown that the advantages of the fluoride ion, when added to 0.025N HCl to control selective extractability of P, did not apply simultaneously to Ca unless the pH of the extractant was held below about pH 2.9. To achieve this objective in calcareous soils either a wide soil: extractant ratio or a considerable higher buffer capacity is required than is inherent in Bray 1. An extractant having the composition 0.2N NH_4Cl , 0.2NHOAc, 0.015N NH_4F and 0.012N HCl at approximately pH 2.5, was reported by Mehlich to offer the desirable buffer properties for the simultaneous extraction of P and Ca from rock phosphate and soils (Mehlich, 1978, 1984).

Mehlich no. 3 (M 3) reagent

Mehlich 2 reagent was modified to include copper among the extractable nutrients, and minimize its corrosive properties. This was accomplished by substituting nitrate for chloride anions and the addition of EDTA. Thus, Mehlich 3 (M3) is composed of 0.2N CH_3COOH , 0.25N NH_4NO_3 , 0.015N NH_4F , 0.013N HNO_3 and 0.001M EDTA buffered at $\text{pH } 2.5 \pm 0.1$. Mylavarupu and co-workers in 2002 demonstrated that mean extracted concentration of K, Mg, and Zn were not significantly different between M-1 and M-3 procedures for all the samples (LSD, $p=0:05$). Larger amounts of micronutrients can be extracted using M-3 solution as it contains dilute acids and EDTA. The higher amounts of Mn, Zn, and Cu extracted by M3 could be attributed to the addition of EDTA that resulted in solubilizing oxidized and organic forms of those nutrients. Mehlich found that addition of EDTA to the M-3 solution increased the Cu, Mn, and Zn by 170%, 50%, and 25% compared to the extracting solution without EDTA addition.

Lacunae of M-3 extractant

NO_3 -N cannot be evaluated with Mehlich 3 because the extractant contains NO_3 -N; fluoride ions in the Mehlich 3 extractant may dissolve K from the glass bottles, and EDTA in Mehlich 3 precipitates after prolonged storage; the correlation coefficients were low for the values of the Mn, Zn, and Cu micro-nutrients extracted with the Mehlich 3 method and the values of those extracted with conventional methods (Masashi, 2000).

Modification of Mehlich 3 to estimate NO_3 -N (Masashi Yanai, 2000)

To determine NO_3 -N, the composition and concentration of the Mehlich 3 extractant was modified. This extractant consisted of $0.2 \text{ mol L}^{-1} \text{CH}_3\text{COOH}$, $0.25 \text{ mol L}^{-1} \text{NH}_4\text{Cl}$, $0.005 \text{ mol L}^{-1} \text{C}_6\text{H}_8\text{O}_7$ (citric acid), and $0.05 \text{ mol L}^{-1} \text{HCl}$ (pH 1.3). Ammonium chloride was used instead of NH_4NO_3 . One percent citric acid method enables to extract soil P that reflects the amount of available phosphorus with a wide range of phosphate absorption coefficients (Uwasawa and Uchida, 1982). The correlation coefficient between the amount of available P extracted with the Truog method and that extracted with 0.005 mol L^{-1} citric acid was 0.99^{***} . The amount of HCl added to the extracted soil nutrient was found to be equal to that by the conventional HCl method. The pH of the solution decreased from 2.5 in Mehlich 3 to 1.3 in this method and thereby the values of extracted copper, zinc and Manganese increased.

AB-DTPA method

For simultaneous extraction of NO_3 , P, K, Zn, Fe, Cu and Mn from alkaline soils, a new extraction solution of 1 M ammonium bicarbonate (NH_4HCO_3), 0.005 M Diethylene Triamine Pentaacetic Acid (DTPA) at a pH of 7.6 was developed (Soltanpour and Schwab, 1977). A high degree of correlation was observed between AB-DTPA method and the standard methods of extraction. The regression equations between AB-DTPA and the standard methods allows one to calculate index values of nutrients in soils. Trehan and Grewal (1985) experimented on different soils across various climatic regions in India to find out the suitability of AB-DTPA in Indian soils and found that for alluvial soils highest correlation was found for P and lowest for Mg. Pradhan *et al.*, (2015) found out the relationship of extractable Cu and Zn with important physico-chemical proper-

ties of soil. The amount of copper extracted by the four extractants showed a significant positive correlation with organic carbon which indicates that the extractable copper content of the soil would increase with increasing organic carbon. DTPA-Cu showed a significant negative correlation with soil pH while, Mehlich 3-Cu had a significantly positive correlation with pH. The highest correlation coefficients were found between DTPA and 0.01 M CaCl_2 ($r = 0.90$), DTPA and 0.01 M BaCl_2 ($r = 0.87$), DTPA and 0.02 M SrCl_2 ($r = 0.86$), DTPA and 0.1 M BaCl_2 ($r = 0.89$) and DTPA and AB-DTPA ($r = 0.85$). (Bibiso *et al.*, 2015). Thus AB-DTPA works as a most suitable universal extractant for the determination of available manganese in soils.

AAAc-EDTA had higher correlation with AB-DTPA for K extractability. Among methods for micronutrients highest significant correlations were observed between AB-DTPA and DTPA for Cu, Fe, and Zn (Sanjay, 2018). Highly significant correlation between DTPA and ABDTPA extractable Zn was reported by Madurapperuma and Kumaragamage (2008) for acidic lowland rice soils; Elrashidi *et al.*, (2003) for alkaline soils and by Natta for calcareous soils. For K and micronutrients (Fe, Mn and Zn), ABDTPA and standard methods correlated in a similar manner with plant uptake. Based on the works of Malathi and Stalin (2018), it is considered that ABDTPA can be used as an effective multi-nutrient extractant for the simultaneous extraction of P, K, S, Fe, Mn, Zn and Cu in alkaline soils.

Multi-nutrient extraction using coffee percolator principle (Chiranjeev, 2017)

An easily applicable soil extraction method was developed using the coffee percolator principle and the results were in close correlation with those of conventional soil testing methods and with the nutrient uptake of the sunflower and ryegrass used as test crops (Chiranjeev, 2017). Several techniques using cation or anion exchange resins which allow the simultaneous extraction of Ca, Mg, K, Al, Mn and P from soil were assessed. Time required for the analysis of Ca, Mg, K, Mn and P in soil is reduced through the use of resin procedures. This extraction procedure involves multi-element analysers such as the ICP and is suitable for a range of soil characteristics, such as pH, texture, organic matter content, and shows significant relationship between the level of elements and crop response.

Universal extraction reagent with a portable multi-channel photoelectric system (Liuzheng *et al.*, 2020)

A universal extraction reagent consisting of 0.45 M NaHCO₃ and 0.374 M Na₂SO₄ buffered at pH 8.5 in association with a portable multi-channel photoelectric system has been proposed. This method provides useful indication for the rapid determination of available NPK concentrations in neutral and calcareous soil in field. A large number of soil samples were collected from crop planting zones in Henan province of central China for evaluating the effectiveness of this universal extractant. The author also designed a portable multi-channel photoelectric system associated with this universal soil extractant to measure the quantity of elements and to provide reliable concentration of available NPK concentrations in soil extracts. The experimental results showed that available NPK concentrations determined by this method are highly correlated with the laboratory-based methods.

Thus, a reliable multi-nutrient extractant has become the need of the hour in order to sustain the fertility of the soil, to provide a healthy soil to the future generation and to maximise the crop yield and productivity without compromising the nutrient quality of food. The potential utility of multinutrient analysers such as Inductively Coupled Plasma – Optical Emission Spectrometry and Atomic Absorption Spectrometers can be achieved by employing multinutrient extractants in the estimation of soil nutrients.

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