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A SIMPLIFIED METHOD FOR LABORATORY SOIL ANALYSIS

N. Chaouqi[1, 2], M.El Gharous[2], Z.Naceri[3], M.Bouzziri[1]

[1] Laboratory of Applied Chemistry and Environment, FST-University Hassan 1st_Settat, [2] INRA-Settat/ IPNI-North Africa, [3] Maroc-Phosphore (OIS / L / Q)-Safi, Morocco.

* Corresponding Author, Received: 10 August 2016, Revised: 06 Nov 2016, Accepted: 01 Dec. 2016

ABSTRACT : The research goal was to develop a simplified method for estimating the available phosphorus for routine analysis. This study compared the measured Soil-P using the ICP-$NaHCO_3$ with the simplified extraction method (SM-P). The correlation (r=0.99) and the regression(using XLSTAT-Pro) were employed for comparing the data of available phosphorus content in soil samples for a variety of Moroccan soil types, with contrasted physicochemical characteristics: Ali Moumen, Oued Qibane, Ouled Said, Dower Hbata, Dower Lhfaya, and Had Ghoualem (are located using ArcGIS 10.1 and fertiMap). SM-P is most suited for soils with pH >= 7 and $CaCO_3$ content above 5%. In this experiment, several parameters are modified, particle size, the type and degree of mechanical agitation ,the color development solution ([$(NH_4)_6Mo_7O_{24}.4H_2O$]&[K(SbO), $C_4H_4O_6$,$5H_2O$],1 %(w/v) ($C_6H_8O_6$)), and the adaptation of the reading at 860 nm, are improving the accuracy of P analysis, the high correlation of this method with ICP-$NaHCO_3$ content can be an indication for it. The results of this experiment showed that SM-P can be the best method for predicting the available phosphorus, simple, quick, and easy to execute.

Keywords: Fertilizer Phosphate , Extraction Methods, Available Phosphorus, Moroccan Soils

1. INTRODUCTION

One of the first problems that arise while studying soil phosphorus, is the extraction method to apply in order to determine a fertility scale for the cultivated plant. Several authors highlighted that phosphate-based fertilization of soils should take into account the assimilation of P reserves by the roots [1]-[3]. That is why it is necessary to assess the relationships existing between the fraction of the phosphorus likely to be extracted by cultivation and the phosphorus extracted by the traditional chemical methods.

In the field of methods, Dyer (citric acid at 2%) [4], Bray-1(0.03N NH_4F + 0.025N HCl), Bray-2 (0.03N NH_4F + 0.1N HCl), DA-4 North Caroline (0.05N HCl + 0.025N H_2SO_4), Joret–Hébert (ammonium oxalate)[5],Chang and Jackson (sodium citrate+ sodium hydrosulfite)[6], Olsen modified by Dabin ($NaHCO_3$ + NH_4F)[7],Resin HCO_3^-(DOWEX 2-X8,300-800µm), Mehlich (0.015N NH_4F + 0.012N HCl)[8],Desorption Kinetics (IMPHOS),anion exchange resin, isotopic exchange kinetics $^{32}PO_4^{3-}$ and $^{33}PO_4^{3-}$, Olsen method 0.5N $NaHCO_3$, prevails worldwide over the others[9].

The information given by Olsen method is the most relevant with the biological results [10]. The reagents, other than sodium bicarbonate, extracted larger quantities of soil, phosphorus forms or freshly introduced fertilizers, less or non-mobile. Despite the limits observed in the case of acidic soils, these results make one considers that Na HCO_3 is the reagent that reflects the availability of P for the crop in question.

The objectives of this study were (1) to render the extraction method of available phosphorus in soil simpler and quicker for routine analyses using less equipped laboratories, and, (2) to correlate it with crop (cereals and pulses) P uptake in order to be use in P fertilizer recommendations.

2. MATERIEL AND METHODS

2.1 Map situation of soils used in the study:

In Morocco, we distinguish several types of soils that have been developed on different geological substrates and under various climatic and topographical conditions. This study concerned 4 representative soil types; including Vertisols, Calcimagnesiques, Isohumiques, Fertialitiques; and one acid soil. With contrasted physicochemical characteristics (The locations of sampling stations on the ground are located using ArcGIS 10.1 and fertiMap). The soils studied here have been collected from a deepness of 20 cm of thickness from different sites, namely:

Zone of Study

Ali Moumen (AL_5)
Dower Hbata (S_6) : Vertisols ;
Oued Qibane (OQ_3) : Fertialitiques ;
Ouled Said (OS_{11}) & (OS_{10}): Isohumiques;
Dower Lhfaya (S_7): Calcimagnesiques;
HadGhoualem (SA_{19}): Acidic Soil.

2.2 Physicochemical characterization of soils

The collected samples have been dried at a temperature of 40°C for 24 hours, ground and sieved (according to AFNOR 11-464), before passing to the other analysis (Table 1). Analysis have been done in Maroc phosphore Laboratory-OCP, Safi.

Table 1 Physicochemical characterization of soils

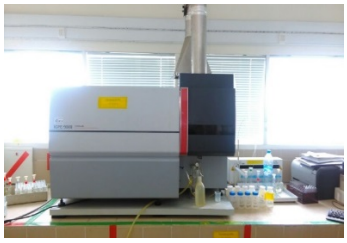
Type / Parameter	OS_{10}	S_6	S_7	SA_{19}	AL_5	OQ_3	OS_{11}
pH	7.1	7.5	7.5	5.1	7.6	7.6	6.9
MO %	3.0	3.78	2.67	1.02	2.61	3.77	3.02
K (ppm)	221	311	282	117	212	669	272
N %	0.29	0.39	0.49	0.41	0.37	0.40	0.37
Ca %	1.27	6.33	5.59	0.14	7.01	6.69	1.23
Al %	10	6.9	1.3	2.6	7.7	7.8	10
Fe %	5	3.5	1.5	1.7	3.8	4.8	5

The majority of the soils are neutral and alkaline, with an average content of Organic matter (2-4%) and a high content of potassium (>200ppm) (This illustration is made according to the reference of International Agro Services, Inc. (ASI).
The table shows us, also, that the Moroccan soils contain a dominance of P-Ca, those results confirm the choice of $NaHCO_3$ for this simplified method.

2.3 Comparison analytical methods used

It is agreed that one or a combination of a validation techniques should be used to determine the performance of a new method, for that, we used (A) and (B), plus, a comparison of the results obtained with other laboratories (Figure 5, in the section concerning results and discussion).

A) - Inductively Coupled Plasma (ICP), ISO 22036, using $NaHCO_3$ as an extracting reagent.



weighing 1 g of soil into a 50 mL Erlenmeyer flask, adding 20 mL of extracting solution (0.5M $NaHCO_3$, pH 8.5) to each flask and shaking at 200 epm for 30 minutes at a room temperature at 24 to 27°C,filtering extracts through Whatman N° 42 filter paper. Analyze for P inductively coupled plasma emission spectroscopy using a blank and standards prepared in Olsen P extracting solution. [11]

B) - Reference Materiel for an Accepted Reference Value (ISO 3534-1), code: P-5.4-MEEV-01.

Parameter	Min	Ref	Max
Fe %	9,15	14,61	20,08
Zn %	2,14	2,63	3,13
K %	316,9	373,44	429,97
EC ms/cm	0,17	0,19	0,22
Ca%	6,32	7,33	8,34
P ppm	140	149	158
N-NO_3%	2,74	2,95	3,16
N-NH_4%	0,39	0,48	0,57
Cl-	6,46	7,23	8,01

The reference materiel received from an accredited Moroccan laboratory, for an accepted Reference Value of phosphorus included between 140 and 158 ppm.

3. RESULTS AND DISCUSSION

3.1 Modified parameters in the P analytical method

A- Extraction phase

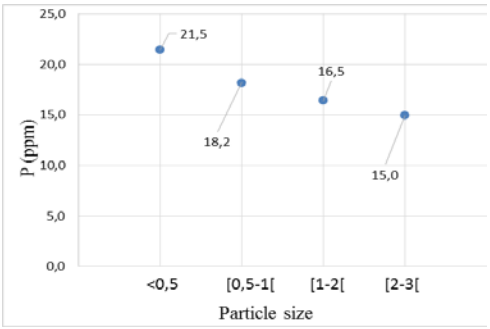


Figure 1 Available P content extracted, based on soil sample particle size.

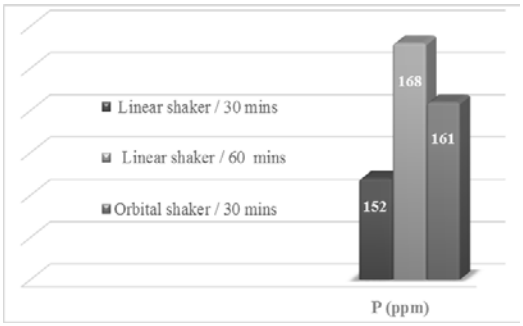


Figure 2 Available P content extracted based on time and type of agitation.

The soil is finely ground in order to increase the specific surface to ensure a good contact and make the reaction as total as possible (Fig 1). The use of a soil with a particle size of 500 µm requires less of $NaHCO_3$, 40 ml for 2.5 g.

Rotation speed fixed at 250 vibrations per minute, this speed is sufficient to allow a good diffusion of reactants for the maximum extraction process of P_2O_5.

B- Color development phase

In this second phase the principles change are at the level of, the color development solution, by separating the Sulfomolybdic ($(NH_4)_6Mo_7O_{24}.4H_2O$) & (K (SbO), $C_4H_4O_6$, $5H_2O$)) to the ascorbic acid solution (1 % (w/v), $C_6H_8O_6$). Then, the adaptation of the reading of the optical density on a spectrophotometer at 860 nm.

3.2 Proposed P analytical method

-Weigh 2.5 g of 0.5 mm of soil into a 250 ml Erlenmeyer flask Add 40 ml of the extracting solution (0.5M $NaHCO_3$, pH 8.5) to the sample,
-Shake 20 minutes (250 vibrations per minute (Orbital shaking))).

- ✓ Sulfomolybdic solution :

Dissolve 60g of [$(NH_4)_6Mo_7O_{24}.4H_2O$], in 1250ml of demineralized water. Dissolve 1.455g of [K (SbO), $C_4H_4O_6$, 5H2O] in 500 ml of demineralized water. Add both of these solutions to 5 L of 5 M H_2SO_4. (148 ml of concentrated H_2SO_4 per L of water),mix and dilute to 10L with demineralized water.
-At completion of shaking time immediately filter the suspensions through sawdust to abtain a clear filtrate.
-To a 5 ml aliquot of the filtrate add 6 ml of sulfomolybdic solution degas by shaking (Hand shaking for 1-2 mins).
-Add 1 ml of 1 %(w/v) ascorbic acid solution.
-Add 13 ml of demineralized water and mix (homogenize carefully by turning).

- ✓ Prepare standards of 0; 0.2 ; 0.4 ; 0.6 ; 1 and 2ppm of P by diluting 0.5 ; 1 ; 1.5 ; 2.5 and 5 ml of the mother solution (Dissolve 0.4393 g of KH_2PO_4 dry at 110°C for 2 hours in 1000 ml of demineralized water) in 250 ml of 0.5M. sodium bicarbonate, pH 8.5(Treat the standards in the same way as the samples).

-Determine P concentration with a spectrophotometer at a wavelength of 860 nm.
Results:
C: Micro-grams of phosphorus determined on the calibration curve (µg/ml)
V: Extraction volume in ml
S: Weight of the soil sample in g.

a. Principle

Alkaline solution reduces the concentration of Ca^{2+} by precipitation in the form of $CaCO_3$ and that of Al^{2+} and Fe^{2+} by precipitation in the form of hydroxides. Phosphate ions concentration increases accordingly and the P may be extracted from the soil sample by the solution of $NaHCO_3$ and filtration.

b. Field of application

This method applies to the determination of available phosphorus in the samples of the Moroccan soil for the different types with pH >= 7.

The combination of this several parameters give as this experimental process, then with it, it was possible to optimize the time of the method in 47 minutes, the temperature effect was replacing by potassium antimony tartrate in the sulfomolybdic solution. The stability problem was also eliminated for this solution, with separating the ascorbic solution to the sulfomolibidc, the wavelength is fixed at 860 nm, which reflects the P content without interference.

3.3 Preliminary comparison of obtained results

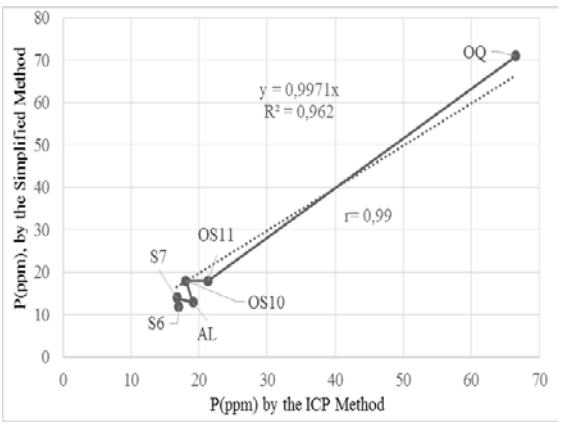


Figure 4 Correlation between ICP and SM-P in relation to the different types of Moroccan soils.

Correlation coefficients (Fig 4) between methods suggest that, the simplified method is comparable to

the ICP method, and this is the same Remarque for the reference materiel, results were nearly identical with a phosphorus value = 146.9 ppm.

The extraction of available P is more dependent on analytical method used; therefore, it is important to come up with a simple and reliable method to be used for routine analyses. For this purpose, we have compared method used by different laboratories in the Mediterranean region to a simplified proposed method.

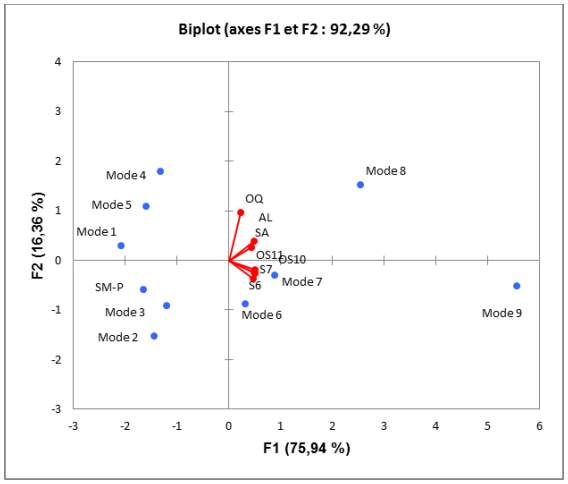


Figure 5 The Comparison with other soil analysis laboratories (n=10/Mode/Soil-Type)

After the comparison with the other laboratories In the Mediterranean region (Fig 5), we observe that there is a Correlation of the several tests, for the value extracted on the different types of soil in the same order (OQ to $S_{(6,7)}$). Then, we could group those who extract more(Mode 9, 8,7,6), and those with a value close to that found by the SM-P(Mode 1,2,3,4,5), this group presents the first future testers of the method (SM-P provides an inexpensive estimate of soil-P, useful compared to their protocols).

Chemical methods, in practice, overestimate the availability of phosphorus of the soils which have much free aluminum[12], whereas it is not the case for this simplified method which is clearly not affected by aluminum, in contrast to ORSTOM method (a modified version of Olsen method referenced by the AFNOR standard under number NF ISO 11263), which, by the action of the fluoride, reacts more actively with the forms related to aluminum.

Concerning the SA_{19} as an acid soil, the comparison of the extracted content of P, is carried out with Bray (pH 1.5), for a P value equal to 104,2ppm.However, It seems that the Bray method extracted a much higher proportion of phosphorus compared to the SM-P with 13 ppm and to the ICP method for 33 ppm.

3.3 Identification of the sources of uncertainties

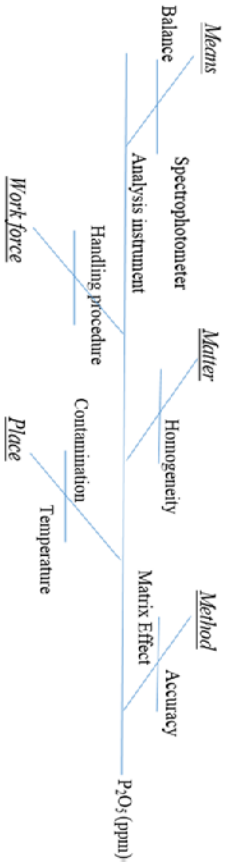


Figure 6 Uncertainties sources, ISHIKAWA Diagram

Determining available P for the Moroccan laboratories has become more instructive while being much easier to obtain. This simplified method constitute an improvement , Taking into account the amount of work that neglected through it compared to currently used methods.
A first analysis (Fig 5) using the SMP allow to exclude certain sources of uncertainties can influence the quantity of the extracted P:

A. Homogeneity and stability

A particle size of 2 mm = 50 %< 500µm + (500µm< 25 %< 1mm) + (1mm< 25 %< 2mm), It cannot ensure the granulomere uniformity, which affects the obtained result. However, sieving with a 500µm ensures homogeneity, and requires less volume of $NaHCO_3$ (40ml/2.5g).

B. Temperature

The molecules of the reagents are within the same phase and can therefore easily enter in contact to react.

This is an independent process of temperature so that it will not affect the reaction speed. However, in all cases it is necessary to take into consideration the T°C control.

C. Extraction solution (pH)

The pH should be close to the conditions of the soil in place. The results obtained for the acid soils by the 0.5M $NaHCO_3$, pH 8.5 are far from those obtained by Bray. Then, regarding the increase of pH: 8.5/1st day, 8.65/2nd day, 8.77/3rd day and 8.94/4th day (Depending on laboratory conditions), the results were not significant (The determined phosphorus content depends on the pH of the extraction solution) [13]. The solution must be kept away from light (pH remains constant for five days). However, a control is necessary prior to any use.

D. Spectrophotometer analysis instrument

Color intensity decreases after 60 min. In addition, it is necessary to add the ascorbic acid solution at appropriately adjusted time intervals to ensure that the readings of the molybdenum blue color intensity, related to each sample, are made about 20 min after the addition of this reagent.

The value of phosphorus read on spectrophotometer, varied with the different Absorption wavelength used. [14]. The 860 nm wavelength was adopted for use in the proposed method because the use of this wavelength always resulted in a standard curve with the lowest slope and highest regression coefficient.

4. CONCLUSION

The results obtained have shown that the outputs of the proposed simplified methods are in concordance with outputs of different P analytical methods used by different laboratories. Therefore, this method could be adopted by a number of laboratories at the level of Mediterranean region.

The SM-P can be recommended for the different types of soil with pH >=7.

Taking into account the amount of work that neglected through this SM-P compared to current methods, as well as the weaknesses of it functioning, namely: Agitation time. The adapting reading at 660 nm, which corresponds at the same time to an interference of soluble organic P. Also, for Arsenates that react with the ammonium, molybdate to form a blue complex producing an interference on the analysis result, plus the problem of P extracted comes from the products of the reaction with phosphatic fertilizers and the ammonium fluoride.
Determining available P for the Moroccan laboratories has become unquestionably more instructive while being easier to obtain.
The simplified method will, however, be further evaluated in the second part of this study by the correlation of its outputs with plant P uptake in order to be used as a basis for P fertilizer recommendations.

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