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The Effects of Three Analytical Systems on the Interpretation of Nutrient "Availability" in Pine Bark Growing Media

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Abstract. An amended pine bark growing medium was extracted for varying lengths of time using modified Spurway, Louisiana State Univ. (LSU), and double acid analytical systems. Concentrations of P, K, Ca, and Mg were then determined in the filtrate. As the extraction time was lengthened, the quantity of P, K, Ca, and Mg removed from the medium increased for each system. The concentration and type of nutrients removed varied according to the composition and action of the extractant.

The interpretation of analytical values regarding nutrient "availability" is dependent on several factors. These include: substrate:extractant ratio, type of extractant used, and length of extraction time. Combined, these factors may be used to create a specific analytical system for various types of growing media.

Although a saturated extract has been recommended for the analysis of soilless growing media (1), this method has not proven satisfactory for media prepared from Southern pine bark. Due to the hydrophobic nature of dried bark particles, a relatively large quantity of extractant is required for "wetting". Once this has occurred, bark readily reacts with the extractant. Because this initial "wetting" process requires a long period of time, the development of a saturated paste is not feasible. Furthermore, by establishing a fixed substrate:extractant ratio, analytical values reflect the concentrations of extracted nutrients without variation in the saturation percentage (5).

The selection of an extractant for substrate analysis must be based on its ability to remove quantities of nutrients that can be related to plant growth. Since no one extractant is suitable for all growing media or all elements, various types have been developed.

The Spurway test (9) has long been con-

sidered the standard soil test for most horticultural crops. This method uses dilute acetic acid (0.025 N HOAc) to remove soluble nutrients from the growth medium. Also, since acetic acid does ionize in solution, at least a small portion of the nutrients extracted by the Spurway procedure are exchangeable.

The LSU analytical system (3) uses neutral normal ammonium acetate (1.0 N NH₄OAc, pH 7) for the extraction of cations. This buffered salt solution removes exchangeable as well as water-soluble nutrients from the growth medium. The effectiveness of this solution has been shown to be limited under extremely acid or alkaline conditions and in the presence of large quantities of organic matter (8).

The LSU system also uses a modified Bray solution (0.1 N HCl + 0.03 N NH₄F) for the extraction of P. This method has been shown to overestimate the quantity of "available" P from various organic sources (2).

The double acid solution (equal parts of 0.05 N HCl and 0.025 N H₂SO₄) is the predominant soil extractant used in soil-testing laboratories throughout the southeastern United States (7). The combination of strong oxidizing and reducing acids in the double acid solution removes exchangeable as well as water-soluble nutrients from the growth medium.

This paper reports on the influence of various analytical extractants on the interpretation of nutrient "availability" in pine bark growing media.

Standardized (National Bureau of Standards sieve no. 4) 25-cc samples of an amended pine bark growing medium (14.27 kg dolomitic lime, 4.09 kg P, and 65.72 g fritted trace elements/m³, respectively) were extracted hourly, for 1 to 24 hr, using modifications of the Spurway, LSU, and double acid analytical systems (1:4 substrate:extractant ratio). The concentrations of K, Ca, and Mg were then determined in the filtrate by means of atomic absorption spectrophotometry (4). P was determined using the molybdovanadate yellow method (5). Each treatment combination was replicated 6 times, and the best-fitting regression model determined.

As the time of extraction was lengthened from 1 to 24 hr, the quantity of P, K, Ca, and Mg removed by each of the 3 systems increased until equilibrium was reached. At that point, the quantity of nutrients removed leveled off even though the length of the extraction time continued to increase. Under these conditions, a 2nd-degree regression equation describes the relationship between extraction times and the quantities of P, K, Ca, and Mg removed by each of the 3 extractants (Tables 1-3).

The solvent action of HOAc used in the Spurway test is designed to simulate the soil solution process. This involves the extraction of water-soluble and some weakly adsorbed nutrients from the bulk solution of the medium. If the activity of these nutrients in the solution phase is decreased, replacement will generally occur from the adsorbed phase. If activity in the solution phase is increased, a shift in equilibrium in the opposite direction usually occurs. Since plants absorb P, K, Ca, and Mg largely from the solution of a growing medium, the modified Spurway method provides good indication of their "availability." However, since not all of the reserve or exchangeable nutrients are measured, the quantity of P, K, Ca, and Mg removed from the bark medium would be expected to be less than that removed by the 2 exchange extractants.

The HCl component of the modified Bray solution, used in the LSU system, is designed to extract acid-soluble Ca, Fe, and Al phosphates, whereas the NH₄F component complexes Al⁺⁺⁺ and Fe⁺⁺⁺ in acid solution.

Table 1. Second-degree equation describing the effect of extraction times on the quantity of element "availability" in pine bark growing medium, as determined by the modified Spurway method.

Element	Equation ^a	R ²
P (ppm)	Y = 6.73 + 1.48X - 0.045X ²	0.670
K (ppm)	Y = 10.89 + 1.32X - 0.040X ²	0.665
Ca (ppm)	Y = 72.11 + 8.56X - 0.255X ²	0.885
Mg (ppm)	Y = 5.62 + 2.30X - 0.067X ²	0.925

^aY = extraction time with a range of 1-24 hr; X = quantity of element availability. All coefficients significant at 5% level.

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Table 2. Second-degree equation describing the effect of extraction times on the quantity of element "availability" in pine bark growing medium, as determined by the modified LSU method.

Element	Equation ^a	R ²
P (ppm)	$Y = 11.19 + 5.450X - 0.15X^2$	0.975
K (meq/100 cc)	$Y = 0.12 + 0.043X - 0.01X^2$	0.891
Ca (meq/100 cc)	$Y = 3.99 + 0.831X - 0.024X^2$	0.930
Mg (meq/100 cc)	$Y = 1.10 + 0.132X - 0.0039X^2$	0.945

^aY = extraction time with a range of 1–24 hr; X = quantity of element availability. All coefficients significant at 5% level.

Since neither Fe nor Al are particularly abundant in bark media, it is likely that Ca phosphate was the predominant P form extracted. However, due to the length of the extraction time, the precipitation of these forms of phosphates may create problems relative to the reproductibility of results.

The extraction of P using the double acid solution also removes acid-soluble forms of phosphate. However, as the HCl and H₂SO₄ components dissociate, Cl⁻ and SO₄²⁻ anions are released. This results in the replacement of H₂PO₄⁻ and HPO₄²⁻ on the exchange complex. Therefore, the quantity of P removed from the bark medium by double acid extraction would be expected to be greater than both that extracted by the modified Spurway and LSU methods.

The net negative charge on bark particles is due primarily to the presence of carboxylic and phenolic groups. As these organic compounds ionize, they produce a negative charge to which cations become covalently bound. The extent of this ionization is largely pH-dependent. Generally, the pH range between

7.9 and 9.0 results in the greatest ionization of carboxylic and phenolic groups (6). The determination of "available" K, Ca, and Mg is thus contingent upon the pH of both the growing medium and the extractant used.

If a bark medium is extracted with a neutral, unbuffered salt solution, only the cations held at active exchange sites are removed. If a buffered solution is used (i.e., 1.0 N NH₄OAc, pH 7.0), the quantity of nutrients removed is influenced by the pH of the extractant. Therefore, the amount of K, Ca, and Mg extracted from the bark medium using the LSU system represents both ions from the bulk solution and those adsorbed to organic radicals. The quantity of exchangeable cations removed was influenced by the effect of pH on the degree of ionization of the carboxylic and phenolic groups.

The dissociation of HCl and H₂SO₄ in the double acid solution results in the release of H⁺ ions. When a bark medium is extracted with the double acid solution, cations are displaced from organic radicals by the pref-

erential adsorption of H⁺. Furthermore, the strong oxidizing and reducing potentials of these two acids increase the quantity of cations released. Since H⁺ ions are adsorbed more readily than NH₄⁺ ions, the quantity of K, Ca, and Mg extracted from the bark medium would be expected to be greater than that removed by neutral normal ammonium acetate.

The results of this experiment indicate that as extraction times were lengthened, the quantities of P, K, Ca, and Mg extracted from the bark medium increased for each of the extractants. This may be attributed to the increased absorption and adsorption of the extracting solutions. The quantity and type of nutrients removed from the bark medium also varied according to the composition and action of each of the 3 systems tested. Therefore, it is essential to consider these factors in the interpretation of analytical results.

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Table 3. Second-degree equations describing the effect of extractant times on the quantity of element "availability" in pine bark growing medium, as determined by the modified double acid method.

Element	Equation ^a	R ²
P (ppm)	$Y = 27.16 + 4.350X - 0.12X^2$	0.922
K (meq/100 cc)	$Y = 0.20 + 0.041X - 0.0012X^2$	0.919
Ca (meq/100 cc)	$Y = 9.44 + 0.212X - 0.006X^2$	0.937
Mg (meq/100 cc)	$Y = 1.06 + 0.126X - 0.003X^2$	0.969

^aY = extraction time with a range of 1–24 hr; X = quantity of element availability. All coefficients significant at 5% level.